I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Thomas Jaramillo, Primary Adviser

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Christopher Chidsey

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Keith Hodgson

Approved for the Stanford University Committee on Graduate Studies.

Patricia J. Gumport, Vice Provost Graduate Education

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Abstract

Electrochemical carbon dioxide reduction reaction (CO$_2$RR) is a promising way to store energy from intermittent electricity sources (ie. wind and solar) and for the synthesis of carbon-based compounds that are currently derived from fossil fuels. To commercialize this process, catalysts that selectively reduce CO$_2$ at low overpotential are needed. Research in this area is hindered by the experimental difficulty of comparing catalyst activity. This thesis begins with the development of a custom electrolysis cell that can be coupled to product detection with NMR and GC. This method allows for accurate voltage measurement and the quantification of all possible products to give the most complete characterization of CO$_2$RR activity available to date. The CO$_2$RR activity of Cu metal is well-studied, but application of this more sensitive experimental method lead to the identification of five novel products: glyoxal, glycolaldehyde, ethylene glycol, hydroxyacetone, and acetone. The CO$_2$RR product identities and their potential dependence inspired the hypothesis that the enol and diol forms of the products may be the active intermediate species on the electrode surface. CO is believed to be an intermediate of CO$_2$RR to methane and ethylene and the direct electrochemical reduction of CO confirmed that it is also a possible intermediate in the formation of many of the novel products observed as well.

After Cu, the activity of Au, Ag, Zn, Ni, Pt, and Fe for CO$_2$RR was also measured using the same experimental method. This represents the most complete dataset of transition metal activity available and reveals several important trends. A plot of CO$_2$RR activity vs. CO binding energy places Au at the top of the volcano, suggesting that it has a near optimal binding energy for CO (and other intermediates) within the pure metals. A strong CO binding energy is also correlated with an early onset potential for HER and methane/methanol formation.

The widespread use of CO$_2$RR will require a catalyst with higher activity than any of the pure metals. Efforts to improve activity began by alloying Fe and Ni, which are poor overall CO$_2$RR catalysts individually, but do produce hydrocarbon products. Alloying decreased the overpotential of needed for methane formation, demonstrating that alloying is a promising method of catalyst improvement.
Acknowledgements

The Stanford community has been an inspiring and enriching place to pursue graduate research and without the many people and programs that are present here, the results presented in this thesis would not have been possible.

I was the third student to join Prof. Thomas Jaramillo’s lab and the first to work on the electrochemical CO₂ reduction project. Progress was slow at first; it took nearly three years just to develop a robust method to measure catalyst activity, which was frustrating from a results perspective. However, through the entire time, Tom managed to stay upbeat and excited. Tom is an exceptional advisor in many ways, but he especially stands out for his willingness to break new ground and try new things. I never felt limited by experimental cost or conventional wisdom. Tom’s openness to trying new ideas and taking scientific risks was paramount to my own development as an independent researcher and the success of this project.

Before joining the Jaramillo lab, I was also part of Prof. Dmitry Yandulov’s lab for one year. Dima, as we called him, was an extremely dedicated scientist who demonstrated a level of scientific thoroughness that will inspire me for the rest of my career. It was in the Yandulov lab that I began working in catalysis and am thankful to have learned essential elements of the field.

Another one of Tom’s strengths was his ability to assemble a talented group of students and post docs to work in the lab. Zhebo Chen and Yelena Gorlin were the first students and the brunt of ordering and setting up lab equipment fell to them. When I started in the Jaramillo lab, I was happy to benefit from their initial work and from their insights into electrochemistry and catalysis. As more researchers joined, a lab culture of cooperation and trouble-shooting help was established. Within the larger lab group, those of us focused on CO₂ reduction formed ‘Team CO₂’ and worked particularly closely to perfect our experimental methods, maintain shared equipment, and compare and contrast the activity of the different materials we studied. Working as a group we were able to study a wide range of transition metals and gain deeper insights into trends in their activity. Current members of the Team CO₂ include: Etosha Cave, David Abram, Toru Hatsukade, Jeremy Feaster, Jakob
Kibsgaard, Chris Hahn, and Sam Fleishman. In addition, I have also been lucky to work with other members of the lab (past and present): Blaise Pinaud, Jesse Benck, Linsey Seitz, Ben Reinecke, Desmond Ng, Ariel Jackson, Pong Chakthranont, Tommy Hellstern, Ieva Narkeviciute, Maureen Tang, Sung-Hyeon Baeck, Paolo Suarez, Arnold Forman, Arindom Saha, Shin-Jung Choi, and Peter Vesborg. Not only was this an amazing group of co-workers, but they also became friends.

The Global Climate and Energy Project of Stanford University provided funding for this project and many opportunities to interact with other researchers in the area of alternative energy. Particularly useful to me was the opportunity to speak in their summer student seminar series and again at the larger fall GCEP conference. Through the GCEP grant, we worked together with Prof. Jens Norskov, Prof. Anders Nilsson, and their respective labs. Their thinking and the work of researchers working in the Norskov lab (Andy Peterson, Heine Hansen, Joey Motoya, Chuan Shi, and Joel Varley) guided our understanding and the search for CO$_2$ reduction catalysts.

I also had the opportunity to work with a number of talented undergraduates: Stephanie Cai, Abrahim El Gamal, and Parth Patel. They helped lay the foundation for future work on novel catalysts.

In addition to those who had a scientific impact on my graduate school career, I’m thankful for the presence of the many people who supported me on a personal level throughout. My parents, Marylane Pannell and Richard Kuhl, encouraged my education without applying to much pressure, allowing me to choose my own path. I’m also fortunate to have a relatively large extended family who have helped keep me on track through the challenges of the last seven years.

I am also thankful for the many friends at Stanford who have offered commiseration and distractions from work throughout. From department barbecues to the tops of some of California’s highest mountains, I have had excellent companions. Lastly, I would like to thank Luke Oltrogge for his ever questioning mind.
Dedicated to my brother
Walker Pannell Kuhl
(1983-2011)
Publications


# Table of Contents

Abstract ........................................................................................................................... v  

Acknowledgements ....................................................................................................... vi  

Dedication .................................................................................................................... viii  

Publications ................................................................................................................... ix  

Table of Contents ........................................................................................................... x  

Chapter 1. Introduction .................................................................................................. 1  
  1.1 Dissertation Overview .......................................................................................... 1  
  1.2 Collaborations ....................................................................................................... 1  
  1.3 Fossil Fuel Reliance ............................................................................................. 2  
  1.4 Recycling CO$_2$ .................................................................................................... 6  
  1.5 Large Scale Implementation ............................................................................... 9  
  1.6 Current State of the Art in CO$_2$ Reduction Catalysts ....................................... 11  
  1.7 Conclusions ........................................................................................................ 13  
  1.8 References .......................................................................................................... 13  

Chapter 2. Experimental Method ................................................................................. 16  
  2.1 Abstract ............................................................................................................... 16  
  2.2 Introduction ........................................................................................................ 16  
  2.3 Summary of electrolysis method .......................................................................... 19  
  2.4 Electrochemical cell setup .................................................................................. 20  
  2.5 Electrolysis method ............................................................................................ 22  
  2.6 Voltage measurement ......................................................................................... 23  
  2.7 Gas phase product quantification ....................................................................... 25  
  2.8 Liquid phase product quantification ................................................................... 28  
  2.9 Product detection limits ...................................................................................... 32
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10 Error calculation</td>
<td>33</td>
</tr>
<tr>
<td>2.11 Agreement with literature/benchmarking</td>
<td>36</td>
</tr>
<tr>
<td>2.12 Conclusions</td>
<td>37</td>
</tr>
<tr>
<td>2.13 References</td>
<td>37</td>
</tr>
<tr>
<td>Chapter 3. Copper Activity</td>
<td>39</td>
</tr>
<tr>
<td>3.1 Abstract</td>
<td>39</td>
</tr>
<tr>
<td>3.2 Introduction</td>
<td>39</td>
</tr>
<tr>
<td>3.3 Methods</td>
<td>40</td>
</tr>
<tr>
<td>3.4 Cu surface preparation</td>
<td>41</td>
</tr>
<tr>
<td>3.5 Products of CO$_2$ reduction on Cu</td>
<td>44</td>
</tr>
<tr>
<td>3.6 Current vs. Potential</td>
<td>51</td>
</tr>
<tr>
<td>3.7 Products vs. Potential</td>
<td>53</td>
</tr>
<tr>
<td>3.8 Error</td>
<td>58</td>
</tr>
<tr>
<td>3.9 Mechanistic implications</td>
<td>60</td>
</tr>
<tr>
<td>3.10 Conclusions</td>
<td>64</td>
</tr>
<tr>
<td>3.11 Copyright</td>
<td>64</td>
</tr>
<tr>
<td>3.12 References</td>
<td>65</td>
</tr>
<tr>
<td>Chapter 4. Gas diffusion electrolysis cell development</td>
<td>66</td>
</tr>
<tr>
<td>4.1 Abstract</td>
<td>66</td>
</tr>
<tr>
<td>4.2 Introduction</td>
<td>66</td>
</tr>
<tr>
<td>4.3 Gas diffusion electrode electrolysis cell</td>
<td>68</td>
</tr>
<tr>
<td>4.4 Electrolyte limitations due to ion exchange membrane</td>
<td>76</td>
</tr>
<tr>
<td>4.5 References</td>
<td>80</td>
</tr>
<tr>
<td>Chapter 5. CO electroreduction</td>
<td>81</td>
</tr>
<tr>
<td>5.1 Abstract</td>
<td>81</td>
</tr>
</tbody>
</table>
7.6 Comparison of Fe, Ni, and FeNi alloy ............................................................ 140
7.7 Comparison to UHV and F-T activity .............................................................. 143
7.8 Conclusions ..................................................................................................... 143
7.9 References ........................................................................................................ 144
Chapter 8. Conclusions and Future Directions ......................................................... 145
8.1 Thesis Summary ............................................................................................... 145
8.2 Future Research Directions .............................................................................. 146
List of Tables .......................................................................................................... xiv
List of Figures ........................................................................................................... xvi
Appendix A. Electrolysis cell development ............................................................. 148
Appendix B. Relevant current density for solar fuels .............................................. 151
Appendix C. Standard reduction potentials of CO$_2$RR half reactions ..................... 152
Appendix D. Minimizing metal impurities ............................................................. 155
Appendix E. Metal sulfide catalyzed CO$_2$RR ...................................................... 157
Appendix F. $^{13}$C NMR peaks .............................................................................. 159
Appendix G. Mercury capture ............................................................................... 161
Appendix H. Metal support activity ....................................................................... 165
Appendix I. Metal electrode CVs in RDE setup with and without CO$_2$ ................. 166
Appendix J. H$_2$O vs. D$_2$O based electrolyte ....................................................... 170
List of Tables

Table 1.3.1. Fossil fuel reserves.................................................................5

Table 1.4.1. Equilibrium potentials of selected CO2RR half reactions and water reduction.................................................................8

Table 1.5.1. Production rate based on input power.................................10

Table 1.5.2. Estimated electricity cost for products of CO2RR.................11

Table 2.8.1. NMR peaks of standards. Green highlighting indicates the peak used for quantification.........................................................31

Table 2.9.1. Detection limits for observed products of CO2RR................33

Table 2.10.1. Error in voltage measurement due to variations in total current and R_u between experiments.....................................................36

Table 3.5.1. Products and their reversible potentials of CO2RR products using a Cu metal electrode catalyst.................................................45

Table 3.5.2. Verification of product identification by comparison to known standards.................................................................47

Table 3.8.1. Experimental measurements and error for CO2RR on a Cu surface......57

Table 4.3.1. Permissible electrolyte and ion exchange membrane combinations......79

Table 5.2.1. Factors that favor ethylene or methane formation.....................83
Table 6.2.1. Binding strength of CO and O to each metal surface……………………108

Table 6.7.1. Comparison to CO2RR data from Hori et al…………………………...116

Table C.1. Change in reversible potential if different reactant is used……………….154

Table D.1. Cu impurity levels in metal foils used in CO2RR……………………….155

Table F.1. 13C peaks resulting from 13CO2RR on Cu……………………………….160
List of Figures

Figure 1.3.1. Past and projected world energy consumption and atmospheric CO₂ concentration.................................................................3

Figure 1.3.2. Fossil fuel usage by economic sector and energy source.........................3

Figure 1.3.3. Non-combustive use of fossil fuels.................................................4

Figure 1.4.1. CO₂ recycling.............................................................................6

Figure 1.5.1. Energy efficiency and electricity costs of selected products as a function of overpotential.................................................................9

Figure 2.4.1. Custom CO₂RR electrolysis cell......................................................21

Figure 2.4.2. Effect of CO₂ flow rate on current efficiency.....................................22

Figure 2.6.1. PEIS plot of a Cu electrode in the electrochemical cell at open circuit potential and -2.1 V. The blue triangle indicates the impedance measured at 10 kHz.................................................................................................24

Figure 2.6.2. Change in Ru over the course of 1 hr long electrolysis.......................25

Figure 2.7.1. Gas chromatogram of gas phase CO₂ reduction products...............26

Figure 2.7.2. Hydrogen standards using two different methods.............................27

Figure 2.8.1. NMR spectra of CO₂ reduction products........................................29

Figure 2.8.2. Determination of NMR parameters...............................................29
Figure 3.7.3. Turnover frequency of CO$_2$RR products generated with a Cu electrode catalyst…………………………………………………………………………………………..55

Figure 3.8.1. Plot of current efficiency and partial current density with one standard deviation error bars…………………………………………………………………...57

Figure 3.9.1. Possible pathway for multicarbon product reduction involving the dehydroxylation of enol-like surface intermediates…………………………………..61

Figure 4.2.1. Result of typical initial CO reduction experiment in standard cell with a Cu foil electrode and 0.1 M KOH electrolyte (pH 13)……………………………………..67

Figure 4.3.1. Expanded view of GDE electrolysis cell……………………………………69

Figure 4.3.2. Cu particles dropcast on GDE with a 5 mg loading………………………...70

Figure 4.3.3. Comparison of Al and graphite current collector CO$_2$ reduction in 0.1 M KHCO$_3$ with the a blank GDE containing no metal particles………………………70

Figure 4.3.4. Effect of Cu loading on CO$_2$RR current efficiency in the GDE cell with 0.1 M KHCO$_3$ electrolyte…………………………………………………………….70

Figure 4.3.5. Deactivation of CO$_2$RR throughout electrolysis in GDE cell with 0.1 M KHCO$_3$ electrolyte………………………………………………………………………72

Figure 4.3.6. Effect of KHCO$_3$ electrolyte concentration on CO$_2$RR products on Cu in the GDE cell……………………………………………………………………………73

Figure 4.3.7. Effect of CO$_2$ flow rate through working electrode gas compartment on CO$_2$RR current efficiency on a GDE containing Cu…………………………………..74
Figure 4.3.8. Comparison of CO reduction current efficiency with the dark or light side of a GDE containing Cu particles facing toward the 0.1 M KOH electrolyte.

Figure 4.3.9. Comparison of CO reduction in standard and GDE electrolysis cells with 0.1 M KOH electrolyte.

Figure 4.4.1. Electrolyte limitations due to ion exchange membrane use.

Figure 4.4.2. Junction potential results from electrolyte ion transport through membrane.

Figure 5.4.1. CO reduction current vs. time with Cu dropcast on a GDE in 0.1 M KOH electrolyte (pH 13).

Figure 5.4.2. CO reduction current efficiency and partial current density on a GDE in 0.1 M KOH electrolyte (pH 13).

Figure 5.4.3. Comparison of CO and CO$_2$ reduction product selectivity on a GDE in 0.1 M KOH electrolyte (pH 13).

Figure 5.4.4. Products of CO$_2$RR on Cu foil in 0.1 M KHCO$_3$ electrolyte (pH 6.8). Products of CO reduction on a GDE in 0.1 M KOH electrolyte (pH 13) are indicated in red.

Figure 5.4.5. Current and product onset potential for CO and CO$_2$ reduction on an RHE and SHE voltage scale.

Figure 5.4.6. Comparison of CO (0.1 M KOH) and CO$_2$ (0.1 M KHCO$_3$) reduction products in GDE cell.
Figure 5.4.7. CO reduction in standard cell with 0.1 M potassium phosphate electrolyte (pH 6.8)…………………………………………………………………..91

Figure 5.5.1. CO\textsubscript{2}RR results in 0.5 M KHCO\textsubscript{3} electrolyte on Cu foil in standard electrolysis cell setup ………………………………………………………………...93

Figure 5.5.2. Comparison of CO\textsubscript{2}RR product selectivity with 0.1 and 0.5 M KHCO\textsubscript{3}………………………………………………………………..………………94

Figure 5.5.3. CO\textsubscript{2}RR results in 0.1 M potassium phosphate electrolyte on Cu foil in standard electrolysis cell with no ion exchange membrane …………………………95

Figure 5.5.4. Change in gas phase product distribution over the hour electrolysis in the standard cell with a Cu foil electrode and 0.1 M potassium phosphate buffer. No ion exchange membrane was used, which allows for Pt from the counter electrode to contaminate the Cu working electrode and is likely responsible for ethane formation………………………………………………………………………….…..97

Figure 5.5.5. Initial CO\textsubscript{2}RR activity in 0.1 M potassium phosphate when less Pt contamination due to the lack of anion exchange membrane has occurred…………………98

Figure 5.6.1. CO reduction results compared to data from Hori et al……………….100

Figure 5.6.2. CO\textsubscript{2}RR results in 0.5 KHCO\textsubscript{3} compared to Kanan et al…………...…101

Figure 5.6.3. CO reduction results compared to Koper et al……………………………….103

Figure 5.6.4. Change in product distribution over time on Cu foil using standard electrolysis cell and 0.1 M KHCO\textsubscript{3} at low overpotentials ………………………………104

Figure 5.6.5. CV before and after CO\textsubscript{2} electrolysis at low overpotential ………….105
Figure 5.6.6. CO$_2$RR current vs time with and without an initial CV ..................106

Figure 6.4.1. Current density and CO$_2$RR current efficiency on each metal.........111

Figure 6.5.1. CO$_2$RR partial current density and moles of CO$_2$ reduced..............112

Figure 6.6.1. Tafel plot and slopes of HER partial current density.......................113

Figure 6.6.2. Tafel plot and slopes of CO$_2$RR partial current density...................114

Figure 6.6.3. Tafel plot and slopes of the total current density during CO$_2$RR experiments..........................................................115

Figure 6.7.1. $^{13}$C incorporation into formate from $^{13}$CO$_2$ reduction...................117

Figure 6.7.2. $^{13}$C incorporation into methanol from $^{13}$CO$_2$ reduction..................118

Figure 6.8.1. Methane and methanol partial current density..............................119

Figure 6.9.1. Volcano plot of a) onset potential of HER, CO$_2$RR, and hydrocarbons and alcohols and b) partial current density for CO$_2$RR at -0.8V vs. CO binding strength.................................................................120

Figure 6.10.1. Comparison of products of CO$_2$RR from Ag, Cu, and Ni...............123

Figure 6.10.2. Selectivity for multi-carbon products...........................................124

Figure 6.10.3. Partial current density of CO$_2$RR products for Ag, Cu, and Ni.........125

Figure 7.2.1. Possible Fischer-Tropsch mechanisms..............................129
Figure 7.3.1. CO$_2$RR electrolysis current on Fe.................................131

Figure 7.3.2. Comparison of Fe CV and average electrolysis current...............131

Figure 7.3.3. CO$_2$RR partial current density and current efficiency for Fe........132

Figure 7.4.1. CO$_2$RR electrolysis current on Ni......................................134

Figure 7.4.2. Comparison of Ni CV and average electrolysis current...............135

Figure 7.4.3. CO$_2$RR partial current density and current efficiency for Ni........136

Figure 7.5.1. XRD of Ni, Fe, and NiFe alloy supported on Ni foil....................137

Figure 7.5.2. XPS of FeNi alloy compared to pure Ni and Fe..........................138

Figure 7.5.3. CO$_2$RR electrolysis current on FeNi alloy...............................139

Figure 7.5.4. Comparison of FeNi CV and average electrolysis current.............139

Figure 7.5.5. CO$_2$RR partial current density and current efficiency for FeNi........140

Figure 7.6.1. Comparison of Fe, Ni, and FeNi alloy........................................141

Figure A.1. Original electrolysis cell design.............................................148

Figure A.2. Current efficiency achieved with cell shown in A.1.....................149

Figure A.3. Second generation electrolysis cell design...............................150

Figure C.1. Reversible potential of selected CO$_2$RR products on an RHE scale......154

xxii
Figure D.1. XPS on metal electrodes before and after CO₂ electrolysis…………….156

Figure E.1. A) STM of cubanes attached to an HOPG surface with XPS showing changes to the Fe and S signal………………………………………………………………………………157

Figure E.2. Current efficiency of H₂ production during CO₂RR experiments on sulfides………………………………………………………………………………158

Figure G.1. SEM images of full-scale samples, a) unused clean surface, b) used surface covered in deposits, c) regenerated surface showing remaining deposits…..162

Figure G.2. Some XPS of Au surfaces from the full-scale experiments. a) comparison of Hg peaks in the used and regenerated samples showing that regeneration removes most of the Hg b) S peaks associated with the oxidized, higher binding energy SOₓ and the reduced, lower binding energy S²⁻………………………………..162

Figure G.3. Depth profile of the used sample showing that the Hg does not penetrate deeply into the Au………………………………………………………………...…163

Figure G.4. SEM images of representative bench-scale samples. a) Au film is peeling, b) Breaks in the film allow the steel underneath to be oxidized, c) Nitric acid rinsed film, d) and e) bench-scale flue gas exposure does not lead to organic deposits as on f) “used” sample from full-scale experiments. Scale bars are 200 μm………………...164

Figure H.1. Average electrolysis current of materials with low CO₂RR activity……..165

Figure I.1. CVs in different electrolytes using RDE setup…………………………………….167

Figure I.2. Voltage @ -1 mA/cm² current density in different electrolytes………………168

Figure J.1. Current density of CO₂RR on Cu in H₂O and D₂O……………………………170
Figure J.2. Partial current density of CO$_2$RR products formed in D$_2$O……………..171

Figure J.3. Ratio of ethylene to methane in D$_2$O and H$_2$O………………………….172
Chapter 1. Introduction

1.1 Dissertation Overview
This dissertation focuses on the electrochemical reduction of CO₂ on transition metal electrodes, a promising strategy to enable the widespread use of alternative energy sources and for the synthesis of carbon neutral fuels and chemicals. Investigation in this area began with the development of a sensitive and accurate experimental method for measuring catalyst activity (Chapter 2). Chapter 3 discusses the application of these methods to study copper metal and the new products that were observed. Detection of a wider range of products leads to the hypothesis that the mechanistic route to multi-carbon products may be through the enol and diol forms of products containing a carbonyl group.

Chapter 4 describes an electrolysis cell designed to improve the mass transport of a reactant gas to the metal catalyst surface through the incorporation of a gas diffusion layer. Chapter 5 explores application of this new electrolysis cell to the electrochemical reduction of carbon monoxide and compares the results to carbon dioxide reduction. Many factors that affect the outcome of the reaction, such as variation in the electrolyte composition and the electrode surface morphology, are also considered.

The last two chapters expand the study of CO₂ reduction to other transition metals. Chapter 6 highlights trends in transition metal catalyzed CO₂ reduction across metals studied to date: Au, Ag, Zn, Cu, Ni, Pt, and Fe. Carbon monoxide binding energy to the metal surface is a major factor in determining CO₂ reduction activity. Chapter 7 goes beyond studying the pure metals to look at the activity of an FeNi alloy electrode and demonstrates that alloying is an effective method to modify and improve CO₂RR activity. The final chapter discusses unanswered questions in CO₂RR catalysis and areas of further research.

1.2 Collaborations
This work would not have been possible without the contributions from other members of the Jaramillo lab’s carbon dioxide reduction subgroup. We have worked together to optimize our experimental methods for CO₂ reduction and applied those methods to the
thorough study of different transition metals. Etosha Cave explored the activity of Au, David Abram explored the activity of Pt, and Toru Hatsukade explored the activity of Ag and Zn. Studying a range of transition metals using consistent methods made it possible to identify the activity trends discussed in Chapter 6.

In addition, we were fortunate to have regular meetings with Jens Nørskov and his research group to discuss their theoretical efforts to determine the mechanism of CO₂ reduction using DFT calculations. Insights gained in these meetings were instrumental to our understanding of CO₂ reduction and in designing experiments to test and improve the activity of transition metals.

1.3 Fossil Fuel Reliance

Electrochemical CO₂ reduction research is driven by the desire to reduce reliance on fossil fuels and lower greenhouse gas emissions. An increasing amount of energy is required to maintain and improve the current standard of living around the world. The majority of energy consumed relies on the burning of fossil fuels, which increases the concentration of carbon dioxide and other greenhouse gases in the atmosphere. Weather patterns world-wide are already changing¹ as a result, and these changes are predicted to become more serious in future.² Figure 1.3.1 shows recorded³ and projected⁴ increases in world energy consumption (driven largely by the development of non-OECD nations) and the accompanying rise in CO₂ concentration.⁵,⁶
Figure 1.3.1. Past and projected world energy consumption and atmospheric CO$_2$ concentration. The left axis applies to the blue lines and the right axis is for the green lines.

Figure 1.3.2 shows the energy usage of the U.S. by economic sector and energy source. Petroleum, coal, and natural gas account for almost all the energy used in the transportation, industrial, and residential & commercial sectors, with renewable and nuclear energy sources only contributing a meaningfully to electricity generation. Fossil fuels are also utilized in non-combustible applications, mostly for the generation of commodity chemicals used to make a variety of products (Figure 1.3.3).

Figure 1.3.2. Fossil fuel usage by economic sector and energy source.
While the current economy and human lifestyle rely on fossil fuel usage, there are pressing reasons to find other sources of energy and chemicals. In addition to climate change, fossil fuels have other negative effects on the environment, such as air and water pollution, which have a high economic cost and detrimental impact on human health. Dependence on fossil fuels has also been linked to the persistence of authoritarian governments and brought about wars and military actions that cause considerable human suffering and negatively affect the economy. Finally, fossil fuels are not a renewable resource and due to their finite supply, there will eventually be no other choice than to find alternatives. Table 1.3.1 contains the amount of energy in known fossil fuel reserves and the number of years remaining at the current consumption rate of each resource. Table 1.3.1 illustrates that fossil fuels are a limited resource, however it is not possible to accurately know the number of years of supply beyond this rough estimate, due to the discovery of new reserves, cost fluctuations, and shifting consumption trends.
Table 1.3.1. Fossil fuel reserves and years of supply remaining at current consumption rates.

<table>
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<tr>
<th>Fossil Fuel</th>
<th>Proven Reserves (Quad BTU)</th>
<th>Yearly Consumption (Quad BTU)</th>
<th>Years Remaining</th>
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<tr>
<td>Oil</td>
<td>9,380</td>
<td>9.6</td>
<td>97</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>6,520</td>
<td>11.9</td>
<td>55</td>
</tr>
<tr>
<td>Coal</td>
<td>17,200</td>
<td>148</td>
<td>116</td>
</tr>
</tbody>
</table>

While there are compelling reasons to end fossil fuel dependence, cost and a lack of alternatives have largely prevented it. However, the decreasing price of many renewables and the increasingly obvious problems with fossil fuels, will likely lead to more opportunities for alternatives, but the complete replacement of fossil fuels is not easy and likely not technologically possible at this time. The largest reservoirs of untapped alternative energy come from wind\textsuperscript{14,15} and solar,\textsuperscript{16,17} which are more than sufficient to meet world energy demand through electricity generation. Unfortunately, the intermittent nature of these resources limit the fraction of electricity they can supply to the grid without causing instability and power fluctuations.\textsuperscript{16} Optimistic studies put their maximum contribution to the electrical grid around 30%.\textsuperscript{18} In order to increase grid penetration of intermittent renewable resources, they must provide a continuous and stable supply of electricity. This can be accomplished through an efficient energy storage mechanism that can take in energy when excess is available and release it when needed. Unfortunately, no existing energy storage technology is currently capable of accomplishing this task at the necessary scale and cost.

An alternative carbon source for chemicals and carbon-based products is also necessary to end fossil fuel reliance. While there are a number of alternative electricity sources, such as nuclear, geothermal, hydro, wind, and solar, the most accessible alternative source of carbon comes from biomass.\textsuperscript{19-21} While potentially better than fossil fuels, the use of biomass also has a number of drawbacks. Because biomass competes with land currently used for conservation and food producing crops, only a limited amount is available before negative environmental and human health-related
consequences result. These factors will likely restrict the overall use of biomass as a source of carbon-based products. Conversion of CO$_2$ to fuels and chemicals through electrochemical reduction would avoid the problems associated with biomass.

One promising solution to energy storage and for the generation of carbon containing compounds is the use of the carbon in CO$_2$ to make these products. The next section will discuss the advantages of this approach and the varying ways in which it might be accomplished.

### 1.4 Recycling CO$_2$

The conversion of CO$_2$ into fuels and chemicals using energy derived from a renewable source, such as wind or solar, could replace the use of fossil fuels. The conversion of CO$_2$ would offer a way to store energy from intermittent sources indefinitely as a chemical fuel. Energy could be stored in the chemical fuel during times of excess electricity generation and extracted via combustion, or electrochemically (ie. a fuel cell), when the energy output of a wind or solar installation dipped. Carbon-based chemicals could also be generated in this way to replace those that are currently derived from petroleum. Figure 1.4.1 shows the artificial carbon cycle that would be possible if carbon dioxide were electrochemically converted (reduced), which is the focus of this thesis. After electrochemical reduction, other carbon dioxide reduction schemes will also be
discussed: the direct coupling of CO$_2$ reduction to a semiconductor (photoelectrochemical reduction) and the thermochemical reduction of CO$_2$ using hydrogen as in the Fischer-Tropsch reaction and methanol synthesis.

The overall transformation occurring in the electrochemical device in Figure 1.4.1 is:

$$\text{CO}_2 + H_2O \rightarrow C_xH_yO_z + O_2 \quad (1.1)$$

Equation 1.1 is the sum of two electrochemical half reactions. Water oxidation (oxygen evolution reaction, OER):

$$H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1.2)$$

And carbon dioxide reduction reaction (CO$_2$RR):

$$xCO_2 + yH^+ + ne^- \rightarrow C_xH_yO_z + H_2O \quad (1.3)$$

For Equation 1.1 to proceed forward, a significant input of energy is needed, in the form of electrical power, which is converted to energy stored in the chemical bonds of the compounds produced. The equilibrium potentials, which are determined solely by thermodynamics, are given for a subset of possible CO$_2$RR products in Table 1.4.1. Both OER and CO$_2$RR have large kinetic barriers that must be overcome by using catalysts. For both reactions, even with the best available catalysts, excess voltage beyond what is thermodynamically required is needed. This excess voltage is referred to as the overpotential. Lowering the overpotential through the discovery of more active catalysts increases the energy efficiency of producing chemicals and fuels electrochemically through carbon dioxide reduction. While both OER and CO$_2$RR are necessary, this thesis will focus only on the CO$_2$RR half reaction.
Table 1.4.1. Equilibrium potentials of selected CO₂RR half reactions and water reduction.

Equation 1.3 is written in a general form to demonstrate that many carbon-containing products are possible. The actual observed products will depend on several factors, but the identity of the catalyst will play the biggest role. At the same potential as CO₂RR occurs, it is also possible for water to be reduced to make hydrogen (hydrogen evolution reaction, HER); the HER half reaction is also shown in Table 1.4.1. The ideal catalyst would produce only the desired CO₂RR product without concurrent reduction of water.

In electrochemical CO₂RR, the electrochemical reaction is independent of the electricity source. Electricity from wind, solar, nuclear, hydro, or even fossil fuels could be converted into carbon-based products. Another possibility to achieve carbon dioxide electrolysis is to couple catalysts for the reaction directly to the surface of a semiconductor in a photoelectrochemical device. The difficulty of this approach lies in finding semiconductor(s) with the correct properties to generate the voltage necessary to reduce carbon dioxide, in addition to having similar catalyst requirements to electrochemical CO₂RR. Because catalysts requirements are similar between electrochemical and photoelectrochemical CO₂RR, it is possible to develop the catalysts and semiconductors used in this approach separately, so good electrocatalysts discovered through purely electrochemical testing could be applied photoelectrochemically once appropriate semiconductors were available.

Electrochemical CO₂ reduction is not the only way to generate renewable fuels and chemicals. The thermochemical conversion of CO₂ could be another route to renewable fuels. CO₂ can react with H₂ at high temperature and pressure to produce long chain hydrocarbons (Fischer-Tropsch reaction) or smaller molecules (MeOH synthesis).
reaction\textsuperscript{25}). The main barrier to the formation of renewable fuels and chemicals by these thermochemical routes is the production of hydrogen from a renewable source. Ninety nine percent of hydrogen that is currently on the market is comes from fossil fuels, mostly through methane reforming.\textsuperscript{26} The most promising route to renewable hydrogen is water electrolysis. Unfortunately, as is the case with CO$_2$RR, new HER catalysts need to be developed for the commercial production of hydrogen through electrolysis.

Research on both thermochemical and electrochemical CO$_2$RR routes is needed, but the electrochemical route could have several advantages. The reaction could be accomplished in a single step that does not require a high temperature or pressure. This would likely lower the infrastructure costs associated with the process. CO$_2$ reduction could take place in small, portable units, allowing production to be more distributed than thermochemical processing would allow.

1.5 Large Scale Implementation

Figure 1.5.1. Energy efficiency and electricity costs of selected products as a function of overpotential.

The feasibility of CO$_2$ utilization for fuel and chemical synthesis will largely depend on the cost. A major cost associated with CO$_2$RR will likely be the price of electricity. Increasing the energy efficiency of the reaction by decreasing the overpotential, and therefore lowering the amount of electrical energy needed, is a straightforward way to reduce the cost. Figure 1.5.1 shows the increase in energy efficiency and the decrease in
the price paid for electricity that occurs as the overpotential is reduced (assuming 300 mV overpotential for water oxidation).

Scale is also an important factor when considering a process to replace fossil fuels. Figure 1.3.2 shows the extent of fossil fuel reliance. In order to meet demand, an alternative to fossil fuels must have a high production rate. Electrolytic processes are already in use to refine aluminum and in the chlor-alkali process, demonstrating that this type of process is capable of meeting large scale demand. Table 1.5.1 shows how the rate of product formation in an ideal reactor would depend on power input; high production rates could be possible with an optimized device.

<table>
<thead>
<tr>
<th>Production Rate (kg/hr)</th>
<th>100 W</th>
<th>1 kW</th>
<th>100 kW</th>
<th>100 kW</th>
<th>1 MW</th>
<th>10 MW</th>
<th>100 MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>0.046</td>
<td>0.46</td>
<td>4.64</td>
<td>46.4</td>
<td>464</td>
<td>4640</td>
<td>46400</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.027</td>
<td>0.27</td>
<td>2.71</td>
<td>27.1</td>
<td>271</td>
<td>2710</td>
<td>27100</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.011</td>
<td>0.11</td>
<td>1.11</td>
<td>11.1</td>
<td>111</td>
<td>1110</td>
<td>11100</td>
</tr>
<tr>
<td>Methane</td>
<td>0.004</td>
<td>0.04</td>
<td>0.45</td>
<td>4.5</td>
<td>45.1</td>
<td>451</td>
<td>4510</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>0.015</td>
<td>0.15</td>
<td>1.50</td>
<td>15.0</td>
<td>150</td>
<td>1500</td>
<td>15000</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.014</td>
<td>0.14</td>
<td>1.44</td>
<td>14.4</td>
<td>144</td>
<td>1440</td>
<td>14400</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.014</td>
<td>0.14</td>
<td>1.42</td>
<td>14.2</td>
<td>142</td>
<td>1420</td>
<td>14200</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.009</td>
<td>0.09</td>
<td>0.92</td>
<td>9.2</td>
<td>92.3</td>
<td>923</td>
<td>9230</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.008</td>
<td>0.08</td>
<td>0.82</td>
<td>8.2</td>
<td>82.3</td>
<td>823</td>
<td>8230</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.005</td>
<td>0.05</td>
<td>0.50</td>
<td>5.0</td>
<td>49.8</td>
<td>498</td>
<td>4980</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.007</td>
<td>0.07</td>
<td>0.69</td>
<td>6.9</td>
<td>68.8</td>
<td>688</td>
<td>6880</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>0.008</td>
<td>0.08</td>
<td>0.77</td>
<td>7.7</td>
<td>76.9</td>
<td>769</td>
<td>7690</td>
</tr>
</tbody>
</table>

Table 1.5.1. Production rates at different power outputs for an ideal electrolysis reactor.

A common question in CO$_2$RR research is what product is best to make. This will likely depend on the intended application of the products, however, some products are likely to have a higher profit margin than others. Table 1.5.2 shows the electricity cost of producing one metric ton of each product assuming a 300 mV overpotential for CO$_2$RR and OER and compares the cost of electricity to the market price, which is an estimate of
the upper limit of possible profit. Products that are not easily refined from petroleum (formic acid, methanol, ethylene glycol, and 1-propanol) have the highest possible profits. Products that require little fossil fuel processing to make, namely ethylene and methane, have a negative profit margin. This demonstrates how difficult it is to compete cost-wise with fossil fuels and their immediate products. However, changes in the price of electricity, fossil fuels, or government regulations could easily change the relative price of CO$_2$RR derived products compared to those derived from fossil fuels.

<table>
<thead>
<tr>
<th>Product</th>
<th>Market Price $/MT</th>
<th>Yearly World Production MT</th>
<th>Electricity Input kWh/MT</th>
<th>Electricity Cost $/MT</th>
<th>Market - Electricity Cost $</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic Acid</td>
<td>1250</td>
<td>720000</td>
<td>2154</td>
<td>144</td>
<td>1106</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>661</td>
<td>3693</td>
<td>247</td>
<td>605</td>
<td>2728</td>
</tr>
<tr>
<td>Methanol</td>
<td>3333</td>
<td>199540</td>
<td>5517</td>
<td>370</td>
<td>730</td>
</tr>
<tr>
<td>Methane</td>
<td>54</td>
<td>22190</td>
<td>1487</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>889</td>
<td>10700000</td>
<td>6927</td>
<td>464</td>
<td>425</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>1444</td>
<td>6700000</td>
<td>7046</td>
<td>472</td>
<td>972</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>900</td>
<td>907000</td>
<td>10830</td>
<td>726</td>
<td>174</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1004</td>
<td>38870000</td>
<td>12147</td>
<td>814</td>
<td>191</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1289</td>
<td>98863000</td>
<td>20065</td>
<td>1344</td>
<td>-55</td>
</tr>
<tr>
<td>Acetone</td>
<td>1111</td>
<td>60769000</td>
<td>14545</td>
<td>975</td>
<td>137</td>
</tr>
<tr>
<td>Allyl Alcohol</td>
<td>1500</td>
<td>78750000</td>
<td>12717</td>
<td>852</td>
<td>648</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>1543</td>
<td>243167</td>
<td>12495</td>
<td>837</td>
<td>706</td>
</tr>
<tr>
<td>1- Propanol</td>
<td>2390</td>
<td>140000</td>
<td>13004</td>
<td>871</td>
<td>1519</td>
</tr>
</tbody>
</table>

Table 1.5.2. Market price, electricity costs, and maximum profit margin calculated by the difference between the market price and cost of electricity for one metric ton of each CO$_2$RR product considered.

### 1.6 Current State of the Art in CO$_2$ Reduction Catalysts

Much research has focused on ways to improve the energy efficiency of CO$_2$RR and control other important factors, such as selectivity and production rates. The first real breakthrough occurred in 1985, when Hori et al.$^{27}$ discovered that methane and ethylene were the major products when copper metal was used as a catalyst. Since then, a number of reports.$^{28-30}$ have compared the activity of different transition metals and found that the products of CO$_2$RR depend on the binding energy of CO, which is believed to be an
important intermediate in the reduction of CO\(_2\), to the transition metal catalyst used.\textsuperscript{28} Metals that bind CO strongly produce few CO\(_2\)RR products because they are poisoned by CO or other intermediates that form during CO\(_2\)RR; hydrogen from competing water reduction is the main product that is observed. On the other hand, metals that bind CO weakly produce mostly CO as a product, because when CO\(_2\) is reduced to CO, the CO is released from the surface and does not go on to form more reduced products such as alcohols and hydrocarbons. Cu possess an intermediate binding energy for CO, which is believed to be the reason for its unique ability to catalyze the formation of more reduced products that require more than a 2 electron reduction. Unfortunately, none of the materials studied to date for CO\(_2\)RR catalysis possess the necessary activity to be used commercially. An ideal catalyst would operate with a high current density at low overpotential to selectively produce only the desired product. A deeper understanding of the CO\(_2\)RR mechanism and other factors that influence the reaction is needed in order to guide the search for catalysts that meet these criteria.

Work to understand and improve upon the activity of the transition metals for CO\(_2\)RR is ongoing. DFT was used to suggest the mechanism of methane formation on a copper catalyst surface\textsuperscript{31} and uncover trends in onset potential and product selectivity amongst transition metals.\textsuperscript{32} Several reports have dealt with roughened or nano-structured surfaces. Use of a nano-structured copper surface for CO\(_2\)RR shifted the selectivity towards the two carbon products ethylene and ethane;\textsuperscript{33} the onset of CO\(_2\) reduction occurred at a lower overpotential on a similarly structured copper surface;\textsuperscript{34} the selectivity and onset of CO\(_2\) reduction to CO on a gold surface was improved by roughening the gold surface through a series of electrochemical oxidation-reduction cycles.\textsuperscript{35} And development of an electrochemical cell attached to a mass spec allowed for the real-time detection of products and found that copper metal shows unexpected activity for the production of ethylene at low overpotential, although the amount of ethylene was not quantified and the origin of the early onset is not understood.\textsuperscript{36}

While the majority of studies have involved transition metals, a number of other materials have been studied as well. Recently, using ionic liquids in place of aqueous electrolyte was shown to decrease the overpotential necessary for CO\(_2\)RR,\textsuperscript{37,38} however, the current density under these conditions was low. The activity of organic compounds,
such as pyridine, has also been explored and showed selectivity for methanol, a product that is not favored with metal catalysts. The activity of metal-free catalysts has been reviewed. Carbon monoxide dehydrogenase (CODH), a protein, has been shown to convert CO$_2$ to CO at the reversible potential. Expanding upon this work, CODH was tethered to TiO$_2$ to create a photoelectrochemical device capable of CO$_2$ reduction, however, device stability was short lived. Interest in photochemical CO$_2$ reduction has also led to the study of semiconductors as catalysts. The majority of reports, which focus on TiO$_2$, have been reviewed.

1.7 Conclusions
Electrochemical conversion of CO$_2$ to fuels and chemicals is a promising approach to reduce fossil fuel usage. With better catalysts, the process could solve energy storage problems for intermittent electricity sources such as wind and solar; it could also provide a source of carbon-based chemicals. Unfortunately, an ideal catalyst has not been found. This thesis will discuss insights into CO$_2$RR catalysis gained through studying the activity of Cu and a range of other metals using an experimental method with increased accuracy and sensitivity. Hopefully these and other insights will guide the development of improved catalysts.

1.8 References


(24) de Klerk, A. In Fischer-Tropsch Refining; Wiley-VCH Verlag GmbH & Co. KGaA: 2011, p 73.


Chapter 2. Experimental Method

2.1 Abstract
This chapter describes the experimental challenges related to measuring the products of CO$_2$RR and the development of a custom electrochemical reactor to carry out CO$_2$RR experiments coupled to GC and NMR for the detection and quantification of products. A description of commonly use CO$_2$RR methods is given, followed by a summary of the procedure used to generate data presented in this thesis, and an in-depth discussion of individual aspects of the procedure related to the electrochemical cell design, the electrochemical method, voltage measurement, gas and liquid phase product quantification, product detection limits, sources of error, and a comparison to previous literature. The principle advantages of the method presented here are the detection of the minor products of CO$_2$RR to provide a more complete characterization of catalyst activity than previously available and accurate voltage measurement through the use of IR-compensation.

2.2 Introduction
While carbon dioxide reduction reaction (CO$_2$RR) poses a number of challenges, one of the most basic is the experimental difficulty in studying the reaction because of the need to quantify the products. Compared to other well studied reduction reactions, such as hydrogen evolution (HER) where only one product is possible and oxygen reduction reaction where there are two possible products, CO$_2$RR can generate a near infinite range of products containing C, O, and H. For this reason, it is not possible to measure catalyst activity by taking a simple cyclic voltammogram (CV). While the most common products of CO$_2$RR are hydrogen (from competing HER), CO (gas phase), and formate (liquid phase), in order to conduct a thorough study of catalyst activity, methods must be used that can quantify as wide a range of products as possible with reasonable detection limits in both the liquid and gas phase. The diversity of possible products means that it is difficult for a single product quantification method to be used for all products, so multiple methods are normally necessary.
Most methods of chemical detection require that a fairly substantial amount of product must be generated, which in turn leads to the need to draw fairly high total currents compared to most laboratory electrochemical studies. Unfortunately, drawing large currents leads to errors in voltage measurement (discussed in Section 2.6). This voltage error makes it very difficult to compare CO\textsubscript{2}RR data collected in different laboratories using different conditions (temperature, electrolyte, electrode size, reference electrode position). While there has been a push in recent years to find more active CO\textsubscript{2}RR catalysts, relatively little progress has been made, perhaps partially due to the experimental challenges posed.

While some studies of CO\textsubscript{2}RR have been undertaken using simple one-compartment electrochemical cells, this type of cell is not favored, due to the possibility of products of CO\textsubscript{2}RR formed at the working electrode then diffusing to the cathode and becoming reoxidized. Despite the disadvantage of this system, it has been used successfully in some instances. More popular is the H-type electrolysis cell because the separator between the working and counter electrode compartments slows the diffusion of products. This is especially useful for experiments lasting for longer periods of time (hours to days). Disadvantages of the traditional electrolysis cell include the need to have a fairly high electrolyte volume to electrode surface area ratio (usually > 10:1), which makes it harder to attain a high concentration of liquid phase products, and the exposure of the backside of the working electrode to the electrolyte, which can cause voltage differences across the surface of the electrode because the distance to the counter electrode is different at different points. Nevertheless, this is the most common experimental setup because it can be purchased off the shelf and it has been used in many CO\textsubscript{2}RR studies.

More recently, a flow cell has been used to perform CO\textsubscript{2}RR. The constant flow of electrolyte through the cell has the advantage of offering high mass transport of CO\textsubscript{2} to the surface with any electrolyte used, something that can normally only be achieved with a bicarbonate based electrolyte because of its high capacity for CO\textsubscript{2} in the form of HCO\textsubscript{3}\textsuperscript{-}. A flow cell setup has the advantage of good mass transport, but the constant flow leads to a large dilution of any liquid phase products formed, making them difficult to detect unless present in large quantities. It was also possible to
modify the original flow cell with a membrane separating the counter and working electrode sides to allow for the use of different electrolytes. Specifically, ionic liquids were used on the working electrode side to accomplish CO$_2$RR.$^6$

The flow cell concept is in many ways close to that of a fuel cell setup operating in reverse. A fuel cell type reactor would likely have the very low cell resistance and excellent mass transport necessary in an industrial scale device. Unfortunately, attempts to run CO$_2$RR under fuel cell-like conditions have not been very promising, probably because a Nafion membrane was used leading to a very acidic environment where HER dominated.

Another approach, which is distinct from the rest, is to couple an electrochemical cell directly to a mass spectrometer. This is commonly referred to as a differential electrochemical mass spectrometer (DEMS). DEMS has the advantage that products can be detected as the potential is scanned, shortening data collection times and making it possible to see transitory electrochemical processes.$^7$ The disadvantage is the difficulty in setting up the DEMS system, the need to perform extensive calibrations, and the inability to detect products with low volatility.

With the exception of the DEMS, which must be coupled to a mass spectrometer, electrochemical CO$_2$ reduction can be used with a variety of product detection techniques. Gas chromatography (GC) is the most common for gas phase product quantification.$^{1,4,6}$ Liquid phase products can be more difficult to measure because of the large water background signal and the presence of the electrolyte salt. GC has been employed in some cases.$^1$ High pressure liquid chromatography (HPLC) and NMR$^4$ have also been used. Oxidized carbon containing compounds, such as formate, formaldehyde, and oxalate, can be particularly hard to measure and often require a special technique, such as a chemical assay.$^1$

This chapter outlines an experimental method using a custom electrochemical cell along with GC and NMR, which overcomes many of the experimental challenges of CO$_2$RR described so far. The procedure offers the advantages of very low detection limits for minor products compared to previous literature reports and it allows for accurate voltage measurement. The technique is well suited for lab scale experiments.
to characterize catalyst activity and the superior sensitivity allows for the detection of products that have not been previously observed.

**2.3 Summary of electrolysis method**

What follows is an overview of the method used to conduct each electrolysis experiment at a single potential. Starting with clean and dry electrodes and electrolysis cell components, the electrochemical cell was assembled by sandwiching together a backing plate, an aluminum lead, a platinum counter electrode, the counter electrode compartment of the cell, an ion exchange membrane, the working electrode side of the cell, the working electrode made of the material to be studied, an aluminum lead strip (depending on working electrode geometry), and another backing plate. The cell was then bolted together using 12 nylon screws evenly spaced around the perimeter. With the main cell body assembled, the gas inlets at the bottom of the cell were screwed in place, followed by the salt bridge to the reference electrode. The cell was then placed upright and filled with 0.1 M KHCO$_3$ electrolyte. The flow of CO$_2$ through the cell began; the flow through the working electrode compartment was regulated by a mass flow controller and the flow through the counter electrode side was adjusted to approximately match using a needle valve. The gas exhaust lines were put in place; the exhaust from the working electrode side was routed through the GC sample loop and the gas from the counter electrode was vented through a tube with the outlet submerged under water to prevent air diffusing in and provide back pressure to match the working electrode side going to the GC.

Once CO$_2$ purged through the cell and sample loop for a few minutes, a blank was taken with the GC to assure that there was no background signal. Once a clean background was achieved, the electrochemistry began, starting with an impedance measurement to determine $R_u$. The potentiostat then automatically compensated for 85% of the measured $R_u$ during a CV that was collected next. $R_u$ was then measured again and electrolysis began which consisted of a chronoamperometry (CA) experiment at the desired potential, with the potentiostat compensating for 85% of the most recently measured $R_u$. The CA was paused briefly every 3 mins so that another impedance measurement of $R_u$ could be obtained and compensated for. The
measurement of \( R_a \) was performed at the same potential as the CA. One mL aliquots of the exhaust gas from the working electrode side of the cell were injected into the GC at 5 mins, 23 mins, 41 mins, and 59 mins to determine the amount of gas phase products.

After 1 hr of CA, another CV was taken and the electrochemistry stopped. The gas flow through the cell was then turned off and the exhaust gas ports disconnected so that the electrolyte from the working electrode side of the cell could be pipetted into a vial for storage. The counter electrode electrolyte was then discarded and the cell disassembled, rinsed with water, and dried under a flow of argon. The membrane was rinsed with water and placed in a solution of fresh electrolyte. In the next 1-3 days, NMR was performed on the electrolyte samples to determine the amount of liquid phase products present. Using the GC and NMR measurements of the moles of CO\(_2\) reduction products formed and the number of coulombs passed through the cell during the CA, the current efficiency and partial current density of each product was calculated. Multiple electrolysis experiments were conducted at each potential and the average values taken to give the final data.

2.4 Electrochemical cell setup

There is no standard cell for carrying out CO\(_2\) reduction experiments, so it was necessary to design a custom cell. The process went through several iterations which are outlined in Appendix A before settling on a final design. The cell used for the electrolysis measurements presented in this thesis was made from polycarbonate or Kel-F and fitted with Teflon coated silicon o-rings (McMaster-Carr) and is shown in Figure 2.4.1. The cell maintained the working electrode parallel to the counter electrode to achieve a uniform voltage. An anion exchange membrane (Selemion AMV, AGC Inc.) was used to separate the working and counter electrode compartments to prevent the oxidation of reduced CO\(_2\) products, although the membrane did not completely prohibit the passage of the anionic products acetate and formate, which were detected on the counter electrode side of the cell in low concentration after electrolysis. The cell was designed to have a large electrode area (1.8 cm x 3.3 cm) and a small electrolyte volume (9 mL) in each of the two
compartments, along with a gas headspace of approximately 3 mL above the electrolyte on each side of the membrane. CO$_2$ (5.0, Praxair), regulated by a mass flow controller (pMFC, MKS Instruments) at 20 sccm, flowed through the working electrode compartment of the cell during electrolysis and a similar flow rate of CO$_2$ went through the counter electrode side of the cell. CO$_2$ flow through the cell was necessary in order to see large current efficiencies for CO$_2$ reduction products, presumably because of mass transport limitations in a quiescent cell. The flow rate of 20 sccm was chosen to ensure sufficient CO$_2$ transport to the surface while preventing interference from gas bubbles striking the surface. Figure 2.4.2 shows the current efficiency for the main CO$_2$RR products generated with a Cu catalyst over a range of flow rates. The CO$_2$ was humidified with water by passing it through a bubbler before it entered the electrolysis cell in order to minimize the evaporation of volatile liquid phase products. An Ag/AgCl electrode (Accumet) was used as the reference. The distance between the working and reference electrodes was small (0.5 cm) to reduce $R_u$. 

Figure 2.4.1. Custom CO$_2$RR electrolysis cell.
2.5 Electrolysis method

Once the cell was assembled and CO\textsubscript{2} was purging the electrochemistry began. A CV was taken at 50 mV/s before the CA section of each electrolysis experiment in order to ensure the reduction of any surface metal oxide present. In cases where the potential of the CA was more negative than the potential where oxide reduction occurred, then CVs were taken out to the voltage of the CA. When the CA was collected at a voltage less negative than needed to ensure surface oxide reduction, then the CV was taken to a more negative voltage than the CA.

The initial CV was followed by 1 hr of CA at a set potential with the value of $R_u$ updated every 3 mins by running a quick impedance measurement. It was necessary to update the value of $R_u$, particularly at the more negative potential values because the value would decrease over the course of experiment (for more on voltage measurement, see Section 2.6).

After an hour of CA, another CV with the same voltage range and scan rate was collected as the original CV. For the most part, CVs collected before and after the CA experiment matched well. In cases where a slight decrease in the absolute value of the current was observed during the CA, the CV also showed a decrease in current. Section 5.6 discusses the effect of skipping the initial CV in this procedure.
2.6 Voltage measurement

In order to obtain the most meaningful data, an experimental setup must provide accurate electrochemical measurement of the current and voltage while also allowing for product identification and quantification with high sensitivity for all possible products (any organic compound consisting of C, H, and/or O). To generate detectable amounts of products, relatively large currents are necessary. Thus, in this study, current densities in the range of negative 0.5–20 mA cm$^2$ were investigated. Not coincidentally, this current density range is relevant for solar fuel synthesis as 10 mA cm$^2$ of CO$_2$ reduction current matches the solar photon flux for a ~ 10% efficient device under AM1.5G sunlight (see Appendix B for details).

An important consequence of this relatively large magnitude of current is that it can lead to substantial errors in the measurement of voltage due to IR-drop in the electrochemical cell, unless one adequately compensates for the solution resistance, also referred to as $R_u$. Solution resistance causes a voltage drop between the reference electrode and working electrode which follows Ohm’s law:\(^8\)

\[ V = I * R \]  (2.6.1)

This resistance is commonly referred to as uncompensated resistance ($R_u$), because the potentiostat does not compensate for it under normal conditions. $R_u$ is dependent upon a number of factors, such as electrolyte, temperature, electrode placement, and electrode size. Since $R_u$ may differ between experiments, it must be corrected for in order to generate consistent data. For instance, in this experimental setup a value of 15 Ω is typically measured for $R_u$, and with a total current of 45 mA (10 mA cm$^2$) this leads to a 0.72 V difference between the potentiostat reading and the true voltage at the working electrode if IR compensation is not used. This discrepancy between actual and applied voltage requires the use of IR compensation in order to get reproducible data that is comparable between different laboratories and experimental setups.

Potentiostatic electrochemical impedance spectroscopy (PEIS) was used to determine $R_u$. The relationship between an AC potential and the resulting AC current defines the impedance.\(^9\) At high frequency, contributions to the impedance from components of the electrochemical circuit other than $R_u$ become negligible. However, there is a limit to how high of frequency can be used before the measured impedance
no longer applies to the electrochemical cell. To find the correct frequency in determining \( R_u \), PEIS was performed at frequencies ranging from 1 MHz to 1 Hz at open circuit potential and -2.1 V vs. an Ag/AgCl reference electrode. 10 kHz was chosen as an appropriate frequency to determine \( R_u \), which corresponds to the real impedance measured at this frequency (Figure 2.6.1). Subsequent determinations of \( R_u \) were performed only at 10 kHz.

![PEIS plot of a Cu electrode in the electrochemical cell at open circuit potential and -2.1 V. The blue triangle indicates the impedance measured at 10 kHz.](image)

Figure 2.6.1. PEIS plot of a Cu electrode in the electrochemical cell at open circuit potential and -2.1 V. The blue triangle indicates the impedance measured at 10 kHz.

The potentiostat’s IR compensation function was used to compensate for 85% of \( R_u \). It is not possible for the potentiostat to compensate for 100% of \( R_u \) because it gives rise to instability in potentiostat control.\(^{10}\) To get the most accurate numbers, the final 15% of \( R_u \) was mathematically corrected for after the electrochemical data was collected. The adjustment to the voltage was:

\[
V_{100\%\text{ IR corrected vs RHE}} = V_{85\%\text{ IR corrected vs RHE}} - 15\% \times \text{Avg } R_u \times \text{Avg I} \quad (2.6.1)
\]

Figure 2.6.2 shows that at higher overpotential and current, the value of \( R_u \) decreased over the course of the hour long electrolysis. In order to avoid overcompensating for \( R_u \) and to maintain potentiostat stability, it was necessary to remeasure the value of \( R_u \) periodically. A temperature probe placed in the electrolysis cell revealed that at -1.18 V, the most negative potential tested, the temperature of the electrolyte rose by 3° C over the course of the hour and is likely the cause of the decreased resistance. At
lower overpotential and current, \( R_u \) did not decrease during electrolysis, but the value still fluctuated about a mean.

![Figure 2.6.2. Change in Ru over the course of 1 hr long electrolysis](image)

**2.7 Gas phase product quantification**

One mL aliquots of the reactor exhaust were injected via an automated sample loop into a gas chromatograph (GC, SRI 8610C in the Multi-Gas #3 configuration).\(^{11}\) Briefly, the GC ran \( \text{N}_2 \) as a carrier gas to maximize sensitivity for \( \text{H}_2 \) and contained a molecular sieve 13X and a haysep D column which were used together to separate hydrogen, methane, CO, CO\(_2\) and ethylene. After exiting the columns, the gas stream first went through a thermal conductivity detector (TCD) where hydrogen was detected. The gas stream then passed through a methanizer where CO and CO\(_2\) were converted to methane and then flowed directly to a flame ionization detector (FID) where the carbon containing gas products were quantified. The peak areas for hydrogen, methane, CO, CO\(_2\) and ethylene were compared to standards to find the concentration of each. Figure 2.7.1 shows a typical chromatogram with FID and TCD traces.
Exhaust gas aliquots were collected at 5 mins, 23 mins, 41 mins, and 59 mins into the CA to determine the concentration of gaseous products, which included hydrogen, methane, CO, and ethylene. The current efficiency was calculated by determining the number of coulombs needed to produce the measured amount of each product then dividing by the total charge passed during the time of the GC sampling.

\[
\text{Current Efficiency} = \frac{\text{Mol of product} \times e^- \text{ per mol} \times 96485}{\text{Avg } I \text{ at sampling time} \times \frac{60}{\text{Flow rate}}} \tag{2.7.1}
\]

Figure 2.7.1. Gas chromatogram of gas phase CO\textsubscript{2} reduction products
The steady state current efficiency reported at a given potential is the average of the current efficiencies measured at 23, 41, and 59 mins. Electrolysis experiments at each potential were repeated three times, in the same fashion, and the average of the three experiments was reported.

To determine the concentration of products, a single standard of 1000 ppm of CO, methane, ethylene, and ethane with a balance of nitrogen was used to find the peak area/concentration measured by the GC. For hydrogen concentration determination, a more extensive standardization procedure was followed. The electrochemical cell was setup with a Pt working electrode, a phosphate buffer, and N₂ purge gas. A series of different currents were run through the cell and the N₂ leaving the cell sampled with the GC. Under these conditions, it is reasonable to assume that all of the current goes to produce hydrogen and the amount of hydrogen produced can be correlated to the peak area measured by the GC. It was confirmed that the standard curve constructed by the electrochemical generation of hydrogen matched standard curve constructed by mixing known amounts of hydrogen and nitrogen together with MFCs. Figure 2.7.2 shows a standard curve for electrochemically generated hydrogen and dilution of hydrogen made with MFCs.

![Figure 2.7.2. Hydrogen standards using two different methods](image-url)
2.8 Liquid phase product quantification

Liquid phase products were quantified using 1D $^1$HNMR (600 MHz, Varian Inova). NMR is generally not used quantitatively because differences in the T1s of analytes can lead to differing peak areas when measurements are made under differing conditions, such as different number of scans or solution compositions. In addition, there are other factors, such as shimming and phasing that can cause differences in peak areas. Despite these difficulties, we found NMR to be extremely useful for detection of electrochemical products because it could be performed directly on the electrolyte solution without the need to remove the electrolyte ions. To avoid problems arising from the analyte and internal standard having different T1s, the same spectral acquisition parameters were used for all quantification spectra. In addition, solvent suppression was used to decrease the size of the water peak so that the smaller CO$_2$ reduction product peaks were visible. Samples for NMR analysis were prepared by mixing 700 mL of the electrolyte containing CO$_2$ reduction products after an hour long electrolysis with 35 mL of a ~10 mM dimethyl sulfoxide (DMSO) and ~50 mM phenol (internal standards) in D$_2$O for NMR analysis. Figure 2.8.1 shows a typical 1D $^1$H NMR spectrum collected for quantification on a sample containing commercial standards of CO$_2$ reduction products and internal standards. Different values of several parameters were tested to determine the best values. Figure 2.8.2 shows the presaturation pulse sequence used and the changes in the relative integration of peaks as the value of d1, satdly, and nt (number of scans) was varied. For the most part, the integration was insensitive to changes in these parameters. Since increasing the time of d1 or satdly has the same effect of allowing time for T1 relaxation, but increasing the satdly time leads to further solvent suppression, a short d1 of 0.5 s and a longer satdly of 5 s was used. The number of scans to collect for each sample was set to 52 because it allowed for a relatively short collection time of 8:35 mins while giving signal to noise ratios high enough to detect concentrations of products in the 0.1 mM range.
Peak areas of products were compared to internal standards to make standard curves. The internal standards, phenol and DMSO, were chosen because they did not interfere with peaks arising from CO$_2$ reduction products and because of their non-volatility which allowed for use and storage of the same internal standards solution for all of the product measurements in this study without appreciable change in concentration. The area of product peaks to the right of the water peak was compared to the area of DMSO, and the area of product peaks to the left of the water peak was
compared to the area of phenol for preparation of and comparison to standard curves. Figure 2.8.3 shows 2-4 standard curves for each product prepared from purchased standards using the peaks indicated in Table 2.8.1. Different standard curves for the same product are in good agreement with each other, and when normalized to the number of protons in each of the peaks used to construct the standard curves, the slope of the lines are in good agreement. The linearity of the curves and the agreement of their normalized slopes demonstrate that it was possible in this case to accurately determine the concentration of products in the unknown solutions. Acetaldehyde and propionaldehyde were too volatile to make accurate standard curves, so the average slope/proton found from the normalized standard curves was used. It was also taken
Table 2.8.1. NMR peaks of standards. Green highlighting indicates the peak used for quantification.

into account that the diol and keto forms of acetaldehyde and propionaldehyde are present in a 1:1 ratio in solution when calculating the concentration of each. The coulombs needed to produce that concentration of each product was calculated and divided by the total coulombs passed during the CA to determine the current efficiency.

\[
\text{Current Efficiency} = \frac{\text{Mols of product} \times e^- \text{per mole} \times 96485}{\text{Coulombs}_{\text{Total}}} \quad (2.8.1)
\]
\(^1\)H NMR allowed for quantification of most of the possible liquid phase products. There are several possible products that could not be detected with the standard \(^1\)H NMR method outlined above. Oxalate, which is reported as a product of CO\(_2\) reduction in non-aqueous solvent, does not have any non-exchangeable protons, so it cannot be detected with \(^1\)H NMR. And in aqueous solution, the simple aldehydes, glyoxal and formaldehyde, react with water to form diols and the position of the signal arising from these molecules in \(^1\)H NMR is underneath the peak coming from water, so it is not possible to detect. For this reason a small number of electrolysis experiments were performed with \(^{13}\)CO\(_2\) and \(^1\)H and \(^{13}\)C NMR spectra collected on the resulting electrolyte. \(^{13}\)C NMR in these cases allowed for the detection of products that cannot be seen with 1H NMR, such as oxalate and glyoxal. Unfortunately, due to the long data collection times of \(^{13}\)C NMR, it was not possible to quantify products detected in this way. The detection limit is also expected to increase substantially, leading to less sensitive product detection. \(^1\)H NMR run on the products of \(^{13}\)CO\(_2\) reduction was used to confirm that the observed products arose from CO\(_2\)RR instead of from some other carbon source. The peaks in \(^1\)H NMR are split when the hydrogen giving rise to the signal is bonded to a \(^{13}\)C and so it is possible to quantify the amount of the \(^{13}\)C label incorporated into the products by measuring the ratio of the area of the split peak to the unsplit peak.

### 2.9 Product detection limits

With our experimental methodology, the detection limit for each product detected is given in Table 2.9.1. The detection limits for allyl alchol and glyoxal are higher because the peak used for quantification of allyl alcohol is coupled to multiple protons, and glyoxal can only be observed using \(^{13}\)C NMR, which is less sensitive. Formation of a product in quantities below its detection limit cannot be ruled out, however, for most products the NMR procedure used achieves detection limits in the range of 10–100 µA cm\(^2\), which is quite sensitive, particularly for liquid phase products.
Table 2.9.1. Detection limits for observed products of CO₂RR

<table>
<thead>
<tr>
<th>Product</th>
<th>uA/cm² detectable</th>
</tr>
</thead>
<tbody>
<tr>
<td>formate</td>
<td>6.7</td>
</tr>
<tr>
<td>allyl alcohol</td>
<td>381.2</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>19.1</td>
</tr>
<tr>
<td>nPropanol</td>
<td>85.8</td>
</tr>
<tr>
<td>glycolaldehyde</td>
<td>38.1</td>
</tr>
<tr>
<td>methanol</td>
<td>20.0</td>
</tr>
<tr>
<td>acetone</td>
<td>30.5</td>
</tr>
<tr>
<td>hydroxyacetone</td>
<td>33.4</td>
</tr>
<tr>
<td>acetate</td>
<td>15.2</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>47.6</td>
</tr>
<tr>
<td>ethanol</td>
<td>40.0</td>
</tr>
<tr>
<td>propionaldehyde</td>
<td>76.2</td>
</tr>
<tr>
<td>hydrogen</td>
<td>21.3</td>
</tr>
<tr>
<td>methane</td>
<td>2.1</td>
</tr>
<tr>
<td>CO</td>
<td>0.5</td>
</tr>
<tr>
<td>ethylene</td>
<td>3.2</td>
</tr>
</tbody>
</table>

2.10 Error calculation

Multiple measurements were made at each potential to ascertain the repeatability of the experimental method and to reduce the effect of differences in factors such as the surface preparation between experiments. Although there is variation between experiments, it is not unreasonably large. Figure 2.10.1 shows the current efficiency for different products of CO₂RR using a Cu catalyst plotted with error bars corresponding to one standard deviation. The error in current efficiency is largest when small quantities are measured, such as points taken at low overpotential or for minor products, due to errors in product detection. Error in current efficiency is also
larger at high overpotential, which can be attributed to the rise in the uncertainty of the potential due to errors in the voltage due to IR compensation.

![Current Efficiency Error Diagram](image)

**Figure 2.10.1.** Current efficiency error using a Cu electrode.

The error in the current efficiency for each product was taken by finding the standard deviation in current efficiency between the multiple measurements made at the same potential. In cases where only two measurements were made at a potential, the error reported is the difference in the two measurements. The error in the voltage arises from two sources: 1) there is an error in measuring the value of $R_u$ and 2) the true value of the voltages for experiments run at the same potential differ slightly from one another due to differences in the current drawn and the $R_u$ measured and compensated for. Error arising from the first source was calculated by fitting a line to the values of $R_u$ measured over the course of the electrolysis experiment and finding the difference between each $R_u$ measurement and the line (Figure 2.10.2a) and then
finding the standard deviation in these residuals. It was confirmed that the residuals had a Gaussian distribution by plotting the number of measurements in 0.1 Ω intervals and fitting it to a Gaussian curve (Figure 2.10.2b). The value of the standard deviation was 0.23 Ω, which is consistent with literature reports. The error was then calculated by multiplying the standard deviation in $R_u$ by the average current of the multiple experiments at each potential. Error from the second source was taken to be the standard deviation of the voltage values collected at nominally the same potential. Table 2.10.1 shows a typical example of data from four experiments conducted using Cu at the same potential. In each experiment, the same potential is applied on an RHE scale to give data that is 85% corrected for the voltage losses due to $R_u$, but because each experiment had a different average current and average value of $R_u$, the final correction to the voltage to compensate for $R_u$ 100% leads to small differences in the true potential. The voltage errors from both sources are clearly not independent of one another, however, because the relationship between them was unknown, the calculated error from both sources were added together to give the total error. On average, both sources of error contributed evenly to the total error.

Figure 2.10.2. Determination of the error in $R_u$
2.11 Agreement with literature/benchmarking

The activity of Cu metal for CO$_2$RR was determined in order to test the efficacy of the experimental method described here. Cu is one of the most studied catalysts for CO$_2$RR because it produces significant amounts of hydrocarbons. The presence of literature reports describing the activity of Cu and the range of products formed make it a good catalyst to benchmark an experimental method against. The most complete report of the activity of Cu comes from Hori et al., although there are similar reports from other researchers. Figure 2.11.1 shows data reported by Hori et al. compared to data collected using the method outlined above. In general they are in excellent agreement. The same trends are observed; hydrogen, CO, and formate are generated at low overpotential and production of methane and ethylene takes over at higher overpotential. At the highest overpotentials, which is beyond the scope of the data from Hori et al., the current efficiency of methane and hydrogen continue to increase while the current efficiency of ethylene and ethanol decrease. The similarity of the two data sets shown in Figure 2.11.1 confirms that the experimental method outlined in this chapter can be used to make accurate measurements of the voltage and current efficiency for the products of CO$_2$RR and in addition to the data shown, it was possible with this method to identify and quantify other products that had not been previously reported to arise from CO$_2$RR. Further discussion of the activity of Cu will be discussed in more detail in Chapter 3.

<table>
<thead>
<tr>
<th>V vs. RHE 85% IR-Corrected</th>
<th>Avg mA</th>
<th>Avg Ohms</th>
<th>V vs. RHE 100% IR-Corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.208</td>
<td>-53.07</td>
<td>15.50</td>
<td>-1.0784</td>
</tr>
<tr>
<td>-1.208</td>
<td>-46.58</td>
<td>16.98</td>
<td>-1.0831</td>
</tr>
<tr>
<td>-1.208</td>
<td>-50.57</td>
<td>15.72</td>
<td>-1.0825</td>
</tr>
<tr>
<td>-1.208</td>
<td>-48.27</td>
<td>16.57</td>
<td>-1.0818</td>
</tr>
</tbody>
</table>

Table 2.10.1. Error in voltage measurement due to variations in total current and $R_u$ between experiments
2.12 Conclusions

One of the major challenges in studying CO2RR catalysts is difficulty in the experimental determination of catalyst activity. Using the experimental method outlined in this chapter, it is possible to accurately measure the activity of a CO2RR catalyst. The major challenges that needed to be overcome were the generation and quantification of the products of the reaction and the accurate measurement of the potential where these products were formed. It is only with accurate methods to assess catalyst activity that it will be possible to get a better understanding of CO2RR and begin to tackle the more fundamental problems of lowering the overpotential and affecting the selectivity.

2.13 Copyright

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2.14 References


Chapter 3. Copper activity

3.1 Abstract
This chapter discusses new insights into CO$_2$RR on a metallic copper surface, enabled by the development of an experimental methodology with unprecedented sensitivity for the identification and quantification of CO$_2$ electroreduction products. Copper was studied across a range of potentials and a total of 16 different CO$_2$RR products were observed, five of which are reported here for the first time, thus providing the most complete view of the reaction chemistry reported to date. Taking into account the chemical identities of the wide range of C$_1$-C$_3$ products generated and the potential-dependence of their turnover frequencies, mechanistic information is deduced. We discuss a scheme for the formation of multicarbon products involving enol-like surface intermediates as a possible pathway, accounting for the observed selectivity for eleven distinct C$_2$+ oxygenated products including aldehydes, ketones, alcohols, and carboxylic acids.

3.2 Introduction
Copper metal is the only known material capable of catalyzing the formation of significant amounts of hydrocarbons at high reaction rates over sustained periods of time during CO$_2$RR, however, an overpotential of almost 1 V is required and a fairly broad mix of major and minor products is produced, including hydrogen, ethylene, and methane. Although copper is not an ideal catalyst for CO$_2$ reduction, understanding its unique ability to catalyze hydrocarbon formation would aid in the design of new catalysts that are active at a lower overpotential and with better product control.

A number of excellent reviews\textsuperscript{2-4} summarize the literature associated with CO$_2$ reduction on copper. The mechanism of the reaction is not clearly understood, but CO appears to be an important intermediate. Electroreduction of CO leads to a similar product distribution as observed for CO$_2$ reduction,\textsuperscript{5} producing both ethylene and methane. The data suggests that different rate determining steps lead to the production of ethylene and methane from CO. Ethylene formation is favored over methane at lower potentials and different Tafel slopes and transfer coefficients have been
calculated for each product.\(^2\) It is unknown whether CO or a more reduced C\(_1\) species is coupled to make C\(_2\) and longer carbon chain products. Recent work to shed light on the CO\(_2\) reduction mechanism include the use of density functional theory (DFT) to predict intermediates involved in the formation of methane\(^6,7\) and from an experimental standpoint, the use of on-line mass spectrometry to identify the products formed from the electroreduction of various compounds that could be intermediates on the ethylene pathway.\(^8\)

This chapter focuses on CO\(_2\)RR activity of copper metal foil over a range of potentials. The major products observed are in good agreement with past studies, however, three new important observations were found in our study that provide key insight into the surface chemistry and mechanistic aspects of CO\(_2\) reduction on copper: (1) A total of 16 different reaction products were detected – significantly more than any previous study – a number of which were novel products that were for the first time identified and quantified from a copper surface. Of the 16 reaction products detected, 12 of them were C\(_2\) or C\(_3\) species, comprised of a broad mix of oxygenated species including hydrocarbons, ketones, aldehydes, carboxylic acids, and alcohols. (2) Regarding this broad range of different C\(_2\) and C\(_3\) species detected, the partial current density and therefore the turnover frequency (TOF) of these products generally track that of ethylene across the range of potentials investigated. (3) All of the C\(_2\) and C\(_3\) products detected – without exception – could have plausibly been produced via the dehydroxylation of an earlier, less reduced product in its enol or diol form. These observations lead to the hypothesis that the chemistry to generate the wide range of C\(_2\) and C\(_3\) products could occur through an enol-like surface intermediate; the appearance of the many multicarbon oxygenate products can be conveniently explained in this way and might potentially be used as a guide to determining the C\(_1\) and C\(_2\) species involved in C-C bond formation.

### 3.3 Methods

The experimental methodology used to test the activity of Cu for CO\(_2\)RR was the same as described in Chapter 2, except that a slightly older version of the electrolysis cell was used, which had a 1.5 cm x 3 cm electrode surface area and 8 mL of
electrolyte was used to fill the working electrode side of the cell. The Cu electrode surface was prepared as discussed in Section 3.4 and more advanced NMR techniques were used to verify the identity of the observed CO$_2$RR products which is discussed in Section 3.5.

### 3.4 Cu surface preparation

Copper foil (thickness 1.0 mm, Aldrich, 99.999% metals basis) was used as the working electrode. The surface preparation prior to each experiment consisted of mechanically polishing (400G sandpaper, 3M) until no discoloration was visible and then electropolishing in phosphoric acid (85% in H$_2$O, Aldrich, 99.99% metals basis) potentiostatically at 2.1 V vs. a graphite foil (0.13 mm thick, Alfa Aesar, 99.8% metals basis) counter electrode placed at a distance of 1.5 cm. X-ray photoelectron spectroscopy (XPS, PHI Versaprobe) and scanning electron microscopy (SEM, FEI XL30 Sirion) were used to characterize the surface.

Electropolishing helped to ensure the system was free of contaminants so that electrochemical and product measurements could truly be attributed to the activity of copper. SEM images of the copper electrode surface are shown (Figure 3.4.1) after mechanical polishing and subsequent electropolishing, resulting in a smoother surface free of impurities. Electropolishing was performed in the copper ion diffusion limited regime of the CV (Figure 3.4.2) before oxygen evolution begins and before surface roughening can occur. Figure 3.4.3 shows XPS measurements taken before and after electrolysis. The peaks are attributable to only Cu, O, and C, revealing that no metal impurities are present within the detection limits of XPS. The O likely arises from a thin native oxide at the copper surface as well as from adventitious organics which are also responsible for the C signal. The Cu oxidation state is shown to depend upon the electrode treatment, however, all XPS were ex-situ, and it is likely that during the reduction of CO$_2$ the electrode surface is reduced to Cu$^0$. 
Figure 3.4.1. SEM images of the Cu surface before electropolishing, after electropolishing, and after CO₂RR

Figure 3.4.2. Two electrode CV of Cu in 85% phosphoric acid. Vertical line indicates the potential of electropolishing.
The roughness factor of the Cu electrode was determined by measuring the capacitive current at different scan rates. The Cu electrode was electropolished and setup in the electrolysis cell in the same configuration as used for CO$_2$RR experiments, except that the ion exchange membrane was left out. The cell was filled with 0.1 M KHCO$_3$ and purged with CO$_2$. A CV scan was then taken at 50 mV/s to -1.2 vs RHE to remove any surface oxide present on the Cu. The electrode was then cycled between 0.15 V and 0.3 V vs RHE (Figure 3.4.4). The scan rate was increased from 50-1000 mV/s in progressive scans. The absolute value of the current in the middle of the potential range was averaged for the negative and positive going scans and plotted against the scan rate. The slope of a linear fit to the capacitance data was divided by 28 µF/cm$^2$, the reported capacitance value for a flat Cu electrode,$^{12}$ to give the roughness factor of the Cu surface.

**Figure 3.4.3.** XPS of the Cu electrode surface at different stages
3.5 Products of CO$_2$ reduction on Cu

Table 3.5.1 shows the 16 products of CO$_2$ reduction on a copper electrode identified in this work along with structure, number of electrons, and reduction potential at pH 6.8 vs. RHE calculated from tabulated thermodynamic data.$^{16,17}$ Appendix C discusses this calculation and the reasons different authors have reported slightly different reduction potentials for the CO$_2$RR half reactions. Nine of these sixteen products have been commonly reported in previous studies: methane, ethylene, CO, formate, ethanol, n-propanol, allyl alcohol, acetaldehyde, and propionaldehyde.$^{18}$ Acetate$^{19}$ and methanol$^{20}$ are two species that have been identified as products previously, however they have appeared in only a few reports.

Methanol has been reported as a product of electrochemical reduction on a Cu$_2$O surface, but has not been reported previously as a product on metallic Cu surfaces. To verify that the methanol was not produced only at the beginning of the reaction before the native CuO$_x$ surface had been reduced, aliquots of the electrolyte were examined for methanol after 5 minutes and 1 hr. The amount of methanol present after 1 hr was significantly greater than the amount present after 5 minutes, which indicates that methanol was produced throughout the electrolysis, not solely at the beginning (Figure 3.5.1). The production rate of methanol is roughly 4 orders of magnitude less than that of methane, which is consistent with predictions made based on DFT calculated thermodynamics.$^{21}$
Table 3.5.1. Products and their reversible potentials of CO$_2$RR products using a Cu metal electrode catalyst.

<table>
<thead>
<tr>
<th>Product</th>
<th>$n_e$</th>
<th>E</th>
<th>Product</th>
<th>$n_e$</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formate</td>
<td>2</td>
<td>-0.02</td>
<td>Acetaldehyde</td>
<td>10</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>2</td>
<td>-0.10</td>
<td>Ethanol</td>
<td>12</td>
<td>0.09</td>
</tr>
<tr>
<td>Methanol</td>
<td>6</td>
<td>0.03</td>
<td>Ethylene</td>
<td>12</td>
<td>0.08</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>6</td>
<td>-0.16</td>
<td>Hydroxyacetone</td>
<td>14</td>
<td>0.46</td>
</tr>
<tr>
<td>Methane</td>
<td>8</td>
<td>0.17</td>
<td>Acetone</td>
<td>16</td>
<td>-0.14</td>
</tr>
<tr>
<td>Acetate</td>
<td>8</td>
<td>-0.13</td>
<td>Allyl alcohol</td>
<td>16</td>
<td>0.11</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>8</td>
<td>-0.03</td>
<td>Propionaldehyde</td>
<td>16</td>
<td>0.14</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>10</td>
<td>0.20</td>
<td>1-Propanol</td>
<td>18</td>
<td>0.21</td>
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</table>

Figure 3.5.1. Growth of the methanol signal over an hour long electrolysis
The five remaining products in the table, ethylene glycol, glycolaldehyde, hydroxyacetone, acetone, and glyoxal, are oxygenated $C_2$ and $C_3$ products that have never been reported before to the best of my knowledge. Glyoxal and hydroxyacetone are particularly intriguing. They are the $C_2$ and $C_3$ products requiring the fewest number of electron and proton transfers to form. This demonstrates that at least some C-C coupling occurs between $C_1$ species at this early stage of reduction. The other novel products reported here are also less reduced than previously reported products, perhaps shedding light on intermediate species present on the pathway to ethylene and propanol, the most reduced $C_2$ and $C_3$ products detected.

To determine and confirm the identities of the liquid phase CO$_2$ reduction products described in this work, more advanced NMR experiments were performed. A 2D homonuclear correlation spectroscopy (COSY) experiment was employed (800 MHz, Agilent VNMRS) to determine which proton peaks were correlated in the $^1$H NMR spectra. $^{13}$CO$_2$ (99% enriched in $^{13}$C, Isotec) was reduced using the above electrolysis procedure and the resulting $^{13}$C labeled products were subjected to 1D $^{13}$C (500 MHz, Varian Inova) and 2D ($^1$H/$^{13}$C) heteronuclear single-quantum coherence (HSQC) (800 MHz, Varian Inova) NMR experiments. $^{13}$C NMR showed the carbon peaks of products and the 2D HSQC experiment correlated peaks observed in $^1$H spectra to peaks in the $^{13}$C spectra. 1D $^1$H (600 MHz, Varian Inova) and 1D $^{13}$C (500 MHz, Varian Inova) spectra of an authentic sample of each product were matched to the observed CO$_2$ reduction product peaks to verify their identity (Table 3.5.2).

Specific parameters used for 2D NMR spectral collection will now be given. The 2D homonuclear COSY was acquired on an 800 MHz Agilent VNMRS (gCOSY pulse sequence) with prescan magnetization randomization, 1 s water presaturation, over an 8000 Hz spectral width ($t_1$ and $t_2$), 256 ms acquisition time, centered on the water peak for 4 scans per 256 $t_1$ increments. The 2D ($^1$H/$^{13}$C) HSQC experiments (data not shown) were acquired on an 800 MHz Varian Inova (gChsqc pulse sequence). An HSQC of the aliphatic carbon region was acquired with 1 s prescan delay, over 14378 Hz/16089 Hz ($^1$H $t_2$/$^{13}$C $t_1$) spectral widths, $^{13}$C decoupling during 71 ms acquisition time, centered on the water peak ($^1$H $t_2$) and 35 ppm ($^{13}$C $t_1$) for 16 scans per 211 $t_1$ increments. An HSQC of the aromatic carbon region was acquired.
Table 3.5.2. Verification of product identification by comparison to known standards

with 1 s prescan delay, over 14378 Hz/8045 Hz \(^{(1}H \text{ t}_2/^{13}C \text{ t}_1)\) spectral widths, \(^{13}C\) decoupling during 71 ms acquisition time, centered on the water peak \((^{1}H \text{ t}_2)\) and 125 ppm \((^{13}C \text{ t}_1)\) for 8 scans per 96 \(t_1\) increments. A third HSQC of the downfield carbon region (to identify the downshifted formate H-C) was acquired with 1 s prescan delay, over 14378 Hz/8045 Hz \((^{1}H \text{ t}_2/^{13}C \text{ t}_1)\) spectral widths, \(^{13}C\) decoupling during 71 ms acquisition time, centered on the water peak \((^{1}H \text{ t}_2)\) and 165 ppm \((^{13}C \text{ t}_1)\) for 8 scans per 96 \(t_1\) increments.

Using the experimental methodology described in Chapter 2, the detection limit for methane, ethylene, CO, and formate is approximately 10 µA/cm\(^2\) for each product. The detection limit for ethanol, acetaldehyde, acetate, methanol, ethylene glycol, glycolaldehyde, hydroxyacetone, and acetone is approximately 50 µA/cm\(^2\). The approximate detection limit for n-propanol and propionaldehyde is 100 µA/cm\(^2\) while for allyl alcohol and glyoxal it is 400 µA/cm\(^2\). The detection limits for these
latter two compounds are higher because the peak used for quantification of allyl alcohol is coupled to multiple protons, and glyoxal can only be observed using $^{13}$C NMR, which is less sensitive and thus not quantified in this study. Formation of a product in quantities below its detection limit cannot be ruled out; however, for most species this methodology achieves detection limits in the range of 10-100 µA/cm$^2$, which is quite sensitive, particularly for liquid-phase products.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Diol $\rightarrow$ Hydroxyl</th>
<th>Keto $\rightarrow$ Carboxyl</th>
<th>Enol $\rightarrow$ Hydroxyl</th>
</tr>
</thead>
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<td><img src="image" alt="Diagram of Acetaldehyde" /></td>
<td><img src="image" alt="Diagram of Keto" /></td>
<td><img src="image" alt="Diagram of Enol" /></td>
</tr>
<tr>
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<td><img src="image" alt="Diagram of Hydroxyacetone" /></td>
<td><img src="image" alt="Diagram of Keto" /></td>
<td><img src="image" alt="Diagram of Enol" /></td>
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</tr>
<tr>
<td>Acetone</td>
<td><img src="image" alt="Diagram of Acetone" /></td>
<td><img src="image" alt="Diagram of Keto" /></td>
<td><img src="image" alt="Diagram of Enol" /></td>
</tr>
</tbody>
</table>

**Figure 3.5.2.** Equilibrium reactions of the carbonyl containing CO$_2$RR products

A significant fraction of the observed CO$_2$ reduction products are oxygenates. The presence of hydroxyl and/or carbonyl moieties in many of the C$_2$ and C$_3$ products suggests that the C-C coupling step occurs before at least one of the two carbon-oxygen bonds in CO$_2$ is broken. This is different from a Fischer-Tropsch type mechanism previously suggested, in which methylene groups on the surface are responsible for chain growth.$^{22}$ Many of the detected products contain carbonyls, compounds which possess enol tautomers and can undergo hydration in aqueous solution to become diols. These complex equilibria in an aqueous environment make
it difficult to ascertain whether a detected product was released from the electrode surface in that form or whether a different species was released from the electrode and equilibrated to a more stable form once in solution. Figure 3.5.2 shows all the carbonyl containing products in their diol, keto, and enol forms. The most thermodynamically favored form, the one detected by NMR in solution, is indicated in blue and is in agreement with known aldehyde hydration equilibria.\textsuperscript{23-25} Note that the enol tautomer is generally thermodynamically unfavorable in aqueous solution; for example, the difference in $\Delta G^\text{f0}(\text{aq})$ of keto vs. enol form of acetaldehyde is -8.54 kcal/mol.\textsuperscript{26} Thus one would expect a compound desorbing from the electrode in its enol form to quickly convert to its diol and/or keto form.\textsuperscript{27}

It is also important to determine whether or not detected organic species could arise from sources other than CO$_2$ reduction.\textsuperscript{18} To examine this possibility, we conducted a control experiment in which the electrolyte was left overnight in the polycarbonate electrolysis cell with CO$_2$ flowing and no applied potential. No products were detected. The reaction was also run in a cell made of Kel-F® and the same products were observed as those measured from electrolysis in the polycarbonate cell. The incorporation of the $^{13}$C label from the reduction of $^{13}$CO$_2$ can also be used to confirm that products arise of CO$_2$RR because the $^{13}$C causes peak splitting in the $^1$H NMR spectrum. Figure 3.5.3 shows the liquid phase product peaks generated from $^{13}$CO$_2$ reduction on Cu and the resulting peak splitting indicating $>90\%$ incorporation of the $^{13}$C label. Thus, we can confirm that these products do in fact result from CO$_2$RR and not from a contamination source in the electrolysis setup. For a discussion of contamination from metal impurities, see Appendix D.
Recently, it has been pointed out that aldehydes can decompose spontaneously and that their decomposition products can be erroneously assigned as products of the reaction.\textsuperscript{28} To be sure the observed products were stable under electrolysis and storage conditions, an individual solution of each of the carbonyl products was prepared, placed in the electrolysis setup with CO\textsubscript{2} flowing for 1.5 hrs, and then examined by NMR; no decomposition was observed.

### 3.6 Current vs. Potential

Figure 3.6.1a shows the current vs. time profile of a representative electrolysis experiment at each voltage. The current remains stable over the course of the hour at most potentials, indicating little deactivation of the copper electrode due to impurities or otherwise. At -1.18 V vs. RHE, the most negative potential studied, there is a small but noticeable decline in the absolute value of the current over time. The change in current could potentially arise from slight increases in the temperature of the cell at the highest current densities (see Section 2.6), resulting in a modest decrease in the solubility of CO\textsubscript{2}. At the higher current densities, the data becomes somewhat noisy as bubbles begin to form on the electrode surface, which cover areas of the electrode until they grow large enough to be released, causing fluctuations in the current. IR-compensation may also contribute to the changes in current as the bubbles make it more difficult for the potentiostat to maintain a constant voltage.

**Figure 3.5.3.** Splitting CO\textsubscript{2}RR product peaks by $^{13}$C label
Figure 3.6.1b shows the average current for each voltage overlaid with a CV taken before an electrolysis experiment. The current observed during electrolysis matches that of the CV very well, with the slight decrease in current during electrolysis being attributable to bubble formation. The CV shows a prepeak at -0.63 V vs. RHE that has previously been attributed to the onset of CO$_2$ reduction. The reduction of a CuO$_x$ surface species has also been suggested to give rise to this feature. The electrolysis voltages studied herein were all cathodic of this prepeak feature. Measurements anodic of the prepeak are discussed in Section 5.6.

![Figure 3.6.1. Current vs time during CO$_2$RR](image)
3.7 Products vs. Potential

Figure 3.7.1, which plots the current efficiency of each product as a function of potential, is divided into three panels in which major, intermediate, and minor products are grouped. The data is consistent with previously reported data for copper electrodes, however, the data extends to a higher overpotential than previous reports and several new products are reported that have not been detected before.\textsuperscript{4,30} At low overpotentials (before reaching -0.75 V vs. RHE), only hydrogen, CO, and formate are observed. At the lowest overpotentials, Figure 3.7.1 reveals a predominance of hydrogen production over both CO and formate, which are formed at relatively comparable rates. As the overpotential increases, the percentage of the current going to hydrogen evolution decreases while the percent going to CO\textsubscript{2} reduction products increases. At -0.75 V vs. RHE, ethylene and methane are the first hydrocarbons to be observed, with ethylene favored over methane. The current efficiencies for methane and ethylene rise steadily for the next \textasciitilde 200 mV, and at -0.96 V vs. RHE, drastic changes in reaction selectivity are observed. First and most importantly, a significant number of new C\textsubscript{1}-C\textsubscript{3} products begin to emerge. Secondly, the selectivities towards CO and formate begin to decrease slightly. The current efficiencies for all C\textsubscript{2} and C\textsubscript{3} products continue to increase with increasing overpotential, until a peak is reached around -1.05 V (\textpm 0.1 V) vs. RHE. At this potential, the current efficiencies for CO and formate have declined to values close to zero. The current efficiency for H\textsubscript{2} has also been decreasing up to this point, but at -1.05 V vs. RHE, the selectivity for H\textsubscript{2} reverses course and now increases with increasing overpotential. At very high overpotentials, beyond -1.05 V vs. RHE, selectivities towards all C\textsubscript{1}-C\textsubscript{3} products are in decline with the sole exception of methane, whose current efficiency continues to rise along with that of H\textsubscript{2}. Previous reports have not shown current efficiencies at such negative potentials where methane formation is favored so definitively over other CO\textsubscript{2} products, concomitant with increased hydrogen evolution. At the most negative potential investigated in this study, -1.18 V vs. RHE, methane and H\textsubscript{2} account for over 90\% of the current efficiency.

Current efficiency is an important metric by which to understand CO\textsubscript{2} reduction selectivity, however, one must bear in mind that in these plots (Figure 3.7.1)
the total current density is changing significantly across the potential window. Multiplying the total current density at a given potential by the current efficiency for each product allows one to construct a plot of the partial current density going toward the formation of each product vs. potential, shown in Figure 3.7.2. To facilitate the discussion of mechanistic implications, Figure 3.7.2 is grouped differently than in Figure 3.7.1, with three panels showing H₂ & C₁ products, C₂ products, and C₃ products, respectively. As the partial current density for a given product is proportional to its TOF, Figure 3.7.3 shows the data for partial current density converted into an approximate TOF. The TOF is shown in terms of umol·s⁻¹·cm⁻² and molecules ·s⁻¹·surface Cu atom⁻¹ in Figure 3.7.3. The number of surface Cu atoms was used because we do not know the nature of the site that produces each of products. The number of surface atoms was estimated by assuming the atomic density.

**Figure 3.7.1.** Current efficiency of CO₂RR products with a Cu catalyst
of a Cu111 surface with a roughness factor of 2, which results in $3.8 \times 10^{15}$ atoms·cm$^{-2}$. The calculated TOF represents a likely lower bound to the true value, given that repeat measurements of the roughness factor gave values between 1-2 and the true surface is polycrystalline and the calculation of atom density assumes that all of the surface is Cu111, the most dense face. Analyzing reaction rates by means of partial current density can provide a clearer basis by which to understand reaction kinetics.

For example, as described earlier, in the range of -0.7 to -1.0 V the current efficiency plot (Figure 3.7.1) shows a significant decrease in H$_2$. However, the partial current density (Figure 3.7.2) and TOF plots (Figure 3.7.3) show that the rate of H$_2$ formation stays fairly constant in this potential region, and in fact actually increases
slightly (by a factor of 2). Thus, the decrease in selectivity is not due to a decrease in \( \text{H}_2 \) TOF, but rather due to more rapidly increasing TOFs for other products.

Figure 3.7.3. Turnover frequency of \( \text{CO}_2\text{RR} \) products generated with a Cu electrode catalyst

In this same potential region, the partial current densities and TOFs for CO and formate are fairly constant. While this is consistent with previous reports, it is unclear why the TOFs for these products lack a strong potential dependence. Beyond -1.0 V, there is a slight decrease in current producing CO and formate and an increase in current going to \( \text{H}_2 \). \( \text{CO}_2 \) reduction products requiring more than 2 electrons increase in partial current until they reach approximately -1.08 V. After this potential, the current going to all \( \text{C}_2 \) and \( \text{C}_3 \) products decreases sharply, but the current to methane continues to rise within the voltage range measured.
One possible explanation for the difference in the slopes of methane and ethylene as well as for their different behaviors at high overpotential is that there are different rate determining steps leading to each of these products, as suggested in previous studies. Coverage effects could also play a significant role in the measured TOF, as the coverage of certain surface adsorbates are likely to change with applied electrochemical potential, as will be discussed below. While ethylene and methane exhibit different behavior as a function of applied potential, Figure 3.7.2 has another important feature: the partial current densities of all C$_2$ and C$_3$ products track that of ethylene. This is a critical feature with strong mechanistic implications that will be discussed in further detail in Section 3.9.

Of the multicarbon products, ethylene appears the earliest and has the highest current density. Other C$_2$ and C$_3$ products are first detectable at -0.95 V vs. RHE, although it is conceivable that they are present but below the detection limit at less negative potentials. As the overpotential increases, the current going to C$_2$ and C$_3$ products first rises and then falls. Note that in Figure 3.7.2, the absence of a data point for a particular product at a given potential indicates that the species was not observed. We also note that the error in the measurement in some of the minor products (e.g. methanol) can be relatively large due to their low concentration in solution (see Section 3.8), thus for these cases clear trends are not observed.

### 3.8 Error

Measurement error was determined as discussed in Section 2.10. Table 3.8.1 shows the current efficiency and the error (one standard deviation) at each potential. This data was used to add error bars to the current efficiency and partial current density plots, shown in Figure 3.81. While the error in the current efficiency plot seems significant, especially for the minor products, these values translate into only modest error in the partial current density.
### Table 3.8.1. Experimental measurements and error for CO$_2$RR on a Cu surface

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<th>Volts</th>
<th>Formate</th>
<th>Ally Alcohol</th>
<th>Ethylene Glycol</th>
<th>n-Propanol</th>
<th>Glycol-Aldehyde</th>
<th>Methanol</th>
<th>Acetone</th>
<th>Acetaldehyde</th>
<th>Ethanol</th>
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<th>CO</th>
<th>Ethylene</th>
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### Figure 3.8.1. Plot of current efficiency and partial current density with one standard deviation error bars
3.9 Mechanistic implications

From this study, it is clear that Cu catalyzes the formation of a large number of CO$_2$ reduction products, more products than have ever been reported before. Having identified the wide range of products, as well as their partial current densities (i.e. TOFs) as a function of applied potential, one can begin to consider the mechanism of CO$_2$ reduction on a Cu electrode. Any proposed mechanism must account for the formation of all 16 different CO$_2$ reduction products detected in this study. Of these 16 products, the two with the largest current efficiencies are the hydrocarbons methane and ethylene, while the remaining 14 products are oxygenates, 11 of which are C$_2$ and C$_3$ products.

The CO$_2$ reduction products observed at the lowest overpotential, formate and CO, only require a two electron reduction. It is only at higher overpotential that more reduced products are formed. This is consistent with the pervading view that CO and formate have the lowest kinetic barriers to formation. Further reduction of intermediate CO to hydrocarbons is kinetically more difficult, thus the more reduced products appear only at higher overpotentials.$^{5,6}$

As mentioned earlier, the fact that all C$_2$ and C$_3$ products behave similarly as a function of potential is an important clue in deducing mechanistic information. For C-C coupling to occur, favorable reaction energetics are required as well as sufficient surface coverage of the species involved in the coupling reaction. Irrespective of whether the C-C coupling step is a thermochemical step or an electrochemical step, the electrochemical potential can have a significant impact on the rate of C-C coupling. Two C-containing adsorbates must be adjacent to one another for this to occur, and as the electrochemical potential determines which species are present on the surface as well as their coverage, a potential-dependent C-C coupling rate is expected.

It is not surprising that the C-C coupling rate initially increases with increasing overpotential. The subsequent decrease in C-C coupling with further increasing overpotential, however, can be explained by the proton and electron transfers becoming more favorable at negative potentials. At very negative potentials, surface-bound C$_1$ species (e.g. CO, HCO, etc.) are more likely to be reduced all the way to
methane and desorb rather than remain as a surface-bound C_1 intermediate involved in coupling. Therefore, at more negative potentials, the TOF for methane increases while C-C coupling decreases due to the lower statistical probability of the appropriate C_1 intermediates encountering one another, a necessary (but insufficient) condition for C-C bond formation to occur. The same principle applies to C_1 and C_2 intermediates coupling to form a C_3 species.

This view of the surface chemistry for CO_2 reduction can explain why at moderate overpotentials, TOFs for C_1-C_3 products all rise together yet at higher overpotentials, only the TOF for methane continues to rise while the TOFs for all other C_1-C_3 species are in decline. The rise in TOF for H_2 at the more negative potentials is also consistent with an increasing TOF for methane, as proton and electron transfers are heavily favored at such negative potentials. This suggests that either the coverage of adsorbed H is increasing at those potentials or that the Heyrovsky mechanism for H-H bond formation – an electrochemical step – becomes the more dominant pathway for hydrogen evolution.\textsuperscript{31,32}

Thus far, we have been able to mechanistically address the major trends in TOF observed in Figure 3.7.2 for all C_1, C_2, and C_3 products, particularly their rise and/or fall as a function of applied potential. Another major mechanistic question involves the wide range of oxygenated products observed, particularly the eleven C_2 and C_3 species including aldehydes, ketones, carboxylic acids, and alcohols. It is an open question as to how Cu produces such a wide variety of oxygenates; the reaction mechanism must account for such a diversity of products. Ethylene is the only C_2+ hydrocarbon observed, and given the previously mentioned similarities in TOF trends among all C_2-C_3 products, it is plausible that a pathway to ethylene could be common to the C_2+ oxygenates as well. If this is indeed the case, it would suggest that at least one of the two C-O bond breaking steps does not occur until fairly late on the pathway from CO_2 to ethylene, otherwise one would expect fewer oxygenated products among C_2 and C_3 species. Note that this does not discount the possibility of multiple pathways to ethylene existing in parallel.

There are many possible explanations for the wide range of C_2 and C_3 oxygenates observed. One possibility is that there are a wide variety of different sites
on the Cu surface, with each site geared to produce a different product. This is not unreasonable; a surface with more under-coordinated Cu atoms present has been shown to change the product distribution of CO₂ reduction. Another hypothesis is that the same type of surface site can catalyze the formation of a number of different C₁ oxygenates which are thermodynamically accessible at high overpotential, and that these diverse C₁ species can couple to form all of the observed products. If the C-C coupling step between the many possible C₁ intermediates are kinetically accessible, this could certainly explain the wide of C₂+ products observed. Based on these experimental findings, a third and novel hypothesis is also considered: a simple reaction scheme described below in which the same electrochemical step, a dehydroxylation of surface intermediates involving 2 H⁺ and 2 e⁻, is repeated over and over to ultimately produce a wide range of oxygenated products of varying degrees of reduction (Figure 3.9.1). As the free energy pathway for dehydroxylation, which would occur after the rate determining step, is unlikely to differ significantly for various C₂ and C₃ surface intermediates, one can expect the trends in production rates for the various species to follow one another as a function of applied potential. This scheme accounts for all of our experimental measurements, and is based on the fact that many of these multicarbon products possess carbonyl groups with enol tautomers and undergo hydration in the electrolyte.

Figure 3.9.1 shows one plausible reaction pathway which can account for the production of all C₂ and C₃ species observed in this study, bearing in mind the carbonyl equilibria addressed in Figure 3. In this pathway, enol-like intermediates are a major conduit by which C₂ and C₃ products are produced. Intermediates formed on the electrode surface are indicated by orange circles and are drawn in their enol and/or diol form. Blue circles indicate species present in the electrolyte solution as identified by NMR. The pH and protonation state of surface intermediates are unknown, but for simplicity all species are drawn fully protonated. In this scheme, each electrochemical step comes in the form of 2H⁺ and 2e⁻ transfers, leading to a more reduced product by the replacement of a hydroxyl group (which goes on to form water) by a hydrogen atom. Note that while it is unclear which C₁ or C₂ species is involved in the C-C coupling step, the successive dehydroxylation of enol-like surface species is a reaction
In this scheme, after C-C bond formation, the enol-like surface species quickly loses hydroxyls to form ethylene while desorption of intermediates along the way leads to the other observed products. It is hypothesized that the enol-like surface species is kinetically accessible, but not the most thermodynamically stable, so once an intermediate has desorbed, it does not return to the ethylene pathway because it will not re-adsorb in the enol-like configuration. Thus it is expected that the addition of the products observed in this study to the electrolyte would not allow access to the ethylene pathway.

This hypothesis suggests that an enol-like surface species may be key intermediates on the pathway to multicarbon CO$_2$ reduction products. A crucial question remains as to which C$_1$ and C$_2$ surface intermediates are involved in C-C coupling reactions to form C$_2$ and C$_3$ products. Much of the uncertainty comes from not knowing which of the C$_2$ surface species is first to form on the pathway (whether glyoxal forms first or is preceded by another intermediate species that is not detected); likewise the initial C$_3$ species is unknown. Figure 3.9.1 lists possible C$_1$ species present on the electrode based on intermediates from computational studies of CO$_2$
reduction to methane and methanol synthesis on a Cu(111) surface as well as intermediates indicated by in situ Raman spectroscopy during CO₂ reduction. Certainly, further experimental work is needed to fully elucidate CO₂ reduction mechanisms on copper. Hopefully, the results presented here regarding proposed C₂ and C₃ pathways can help guide the search for the C₁ and/or C₂ intermediates involved in C-C coupling.

### 3.10 Conclusions

New insight has been provided on the electrochemical reduction of CO₂ into fuels and chemicals on a Cu electrode surface. A total of 16 CO₂RR products are reported, significantly more than have ever been reported in any previous study on copper. Five of those 16 products are reported here for the very first time.

The products with the largest current efficiencies are the hydrocarbons methane and ethylene, while the remaining 14 products are oxygenates, 11 of which are C₂ and C₃ products. A number of these products are industrial chemicals with global-scale demand on the order of billions of kg/yr. Understanding selectivity for the CO₂ reduction reaction is of paramount importance; to do so, trends in both the current efficiency and the partial current density (proportional to TOF) of each product over a range of potentials were studied.

By analyzing trends in TOF for the multitude of reaction products, important mechanistic information was deduced. As previously observed, methane and ethylene are the dominant products of reaction. Their differing electrochemical behavior over the potential range, however, suggests that they have different rate determining steps. Conversely, the 12 multicarbon products show similarities in their potential-dependent behavior, a key clue in understanding the kinetics of C-C coupling. These 12 multicarbon products include a wide variety of oxygenates, e.g. alcohols, aldehydes, ketones, and carboxylic acids; any proposed pathway must account for similarities in their potential-dependent behavior despite their differences in chemical functionality. To this end, it is suggested that two critical factors can influence the reaction rate and selectivity for C₂⁺ products: (1) coverage effects whereby the coverage and chemical identities of C₁ and C₂ surface species play major roles in determining which C₂⁺
products are formed, and (2) the possibility of reaction intermediates proceeding through enol-like species on the electrode surface, a pathway involving a series of dehydroxylation steps that can account for the wide range of \( \text{C}_2^+ \) oxygenates as well as their simultaneous rise and subsequent fall in TOF, peaking at -1.05 V vs. RHE.

Many unanswered questions still remain as to the specifics of how the electrochemical reduction of CO\(_2\) proceeds on a Cu surface. The results in this chapter, however, provide deeper insight into the reaction chemistry by (1) identifying and quantifying a number of new reaction products previously unreported to form a more complete picture of the reaction chemistry, and (2) using that new information to deduce reaction pathways. With more complete knowledge of the reaction chemistry, one can aspire to design catalysts capable of making desired products selectively and efficiently. The technology to electrochemically convert CO\(_2\) to fuel and industrial chemicals would be a significant step toward a more sustainable future.

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### 3.12 References


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Chapter 4. Gas diffusion electrolysis cell development

4.1 Abstract

Very low current efficiencies were measured for CO electroreduction in the standard electrolysis cell described in Chapter 2. In an effort to increase mass transport of CO to the catalyst surface, a new cell design was developed which utilizes a gas diffusion electrode (GDE) impregnated with metal particles as the working electrode. In addition to mass transport issues, the experimental limits on electrolyte composition and pH are discussed for CO$_2$ and CO reduction.

4.2 Introduction

The electrolysis cell described in Chapter 2 is designed to generated a high concentration of liquid phase CO$_2$RR products and works well for that purpose when CO$_2$ is reduced in 0.1 M KHCO$_3$. However, it is not ideal for the reduction of molecules besides CO$_2$ or for the use of other electrolytes, both of which would allow for interesting experiments to determine if CO or other compounds were possible intermediates in the CO$_2$ reduction pathway and to test the effect of pH and electrolyte composition on CO$_2$RR. The difficulty in reducing compounds other than CO$_2$ most likely arises from differences in mass transport to the catalyst surface. For example, CO does not react with the electrolyte as CO$_2$ does to form bicarbonate and the solubility of CO is low in aqueous solution (1 mM dissolved CO compared to 33 mM dissolved CO$_2$, calculated from Henry’s law constants$^1$). Mass transport is also likely to affect CO$_2$ reduction in electrolytes other than 0.1 M KHCO$_3$ and at lower pH, where the amount of total dissolved CO$_2$ is lower.$^2$ Attempts to electrochemically reduce CO in the standard electrochemical cell setup leads to very low current efficiencies for products compared to those of CO$_2$ (Figure 4.2.1). Such low current efficiencies make it hard to compare the products of CO and CO$_2$ reduction.
Figure 4.2.1. Result of typical initial CO reduction experiment in standard cell with a Cu foil electrode and 0.1 M KOH electrolyte (pH 13).

The need to increase mass transport of CO to the catalyst surface led to the design of a new electrochemical cell, based loosely on a flow cell using a gas diffusion electrode (GDE) designed by the Kenis et al. In this cell design, a GDE containing metal catalyst particles is used as the working electrode. CO\textsubscript{2} gas is flowed on one side of the GDE and the other side faces aqueous electrolyte and the counter electrode. This setup allows for transport of CO\textsubscript{2} in the gas phase to the catalyst surface through the pores in the carbon.

Gas diffusion electrodes are used in fuel cells and metal air batteries to get good mass transport of a reactant gas. A typical GDE consists of porous carbon coated with a hydrophobic polymer. At the cathode of a fuel cell, the pores serve two purposes: to bring oxygen to the catalyst surface and to remove water generated by oxygen reduction. To facilitate water removal and have good electrical conductivity, GDEs often consist of several layers. The side of the GDE that is in contact with the catalyst contains a highly conductive layer of carbon black on top of a layer with micropores. The outer GDE layer in direct contact with the gas consists of larger macropores; this combination of pore sizes helps to keep water from blocking the pores so that oxygen can easily reach the surface. If aqueous electrolyte is used instead of a solid electrolyte in the form of an ion exchange membrane, then the hydrophobicity of the GDE will prevent water from leaking through to the gas side.
The mass transport improvements that come from the use of a GDE in the electrolysis cell described in this chapter are a step towards an electrolysis cell capable of high CO₂ reduction rates. Future efforts are needed to replace the aqueous electrolyte with an ion exchange membrane with higher ionic conductivity in order to reduce overall cell resistance. The most energy efficient cell will most likely resemble the design currently used for water electrolyzers.¹⁰

This chapter introduces the design of the GDE electrolysis cell and preliminary experiments undertaken to determine the best experimental conditions to reduce CO₂ and CO. The second half of the chapter goes on to discuss limitations to the reactant (CO or CO₂) and electrolyte combinations that can be used with an ion exchange membrane without changes to electrolyte pH or concentration.

### 4.3 Gas diffusion electrode electrolysis cell

Figure 4.3.1 shows the GDE cell, which is very similar to the standard cell design, but in the place of a foil working electrode is a GDE containing metal nanoparticles and a third compartment is present on the back side of the GDE for gas flow. The transport of gas to the metal particles is accomplished by bubbling through soln as in the standard cell and by gas diffusing from the gas side of the GDE through pores to the catalyst.
The GDE (Sigracet GDL 35 BC) used was a 325 µm thick sheet of porous carbon paper. The two sides of the GDE were different; one side contained conductive carbon black and was much darker in color, while the other side appeared lighter in color and consisted of intertwined carbon fibers coated with a hydrophobic polymer. Cu was incorporated into the GDE in two ways. The first was by dropcasting a solution of 1:1 IPA:H₂O with 25 mg/mL of Cu nanomaterial (Alfa Aesar, #45504, APS 20-50 nm, 99.9% metals basis) onto the dark side of the GDE. The volume (and sometime concentration) dropcast were varied to deposit more or less Cu. The second method used was the electrodeposition of Cu from a solution of 0.1 M sulfuric acid (Sigma-Aldrich, #339741, 99.999% metals basis) and 0.01 M copper(II) nitrate (Sigma-Aldrich, #229636, 99.999% metals basis) directly into the GDE with its dark side facing the counter...
electrode at -1 V vs. Ag/AgCl. Differing amounts of time and therefore charge were used to vary the loading of Cu onto the GDE. Figure 4.3.2 shows SEM images of Cu nanomaterial dropcast onto a GDE with a 5 mg total loading. It is difficult to see if smaller Cu particles are present due to the roughness of the support, but the images show that at least some of the nanomaterial is agglomerated into large particles.

Figure 4.3.2. Cu particles dropcast on GDE with a 5 mg loading.

In the development of the GDE cell, a number of different experimental conditions were tested for their effect on CO$_2$ reduction in order to determine the best conditions for catalyst testing: current collector material, Cu loading, electrolyte concentration, and flow rate through the gas compartment.

Figure 4.3.3. Comparison of Al and graphite current collector CO$_2$ reduction in 0.1 M KHCO$_3$ with the a blank GDE containing no metal particles.
Aluminum and graphite were considered as possible materials for the current collector. Graphite has the clear advantage of avoiding the addition of another metal to the system, but Al is relatively inactive for CO$_2$RR (see Appendix H). Figure 4.3.3 shows the results of CO$_2$ reduction experiments using a blank GDE with no Cu (dark side to the electrolyte) with an 45 sccm total flow rate (15 sccm through each compartment), 0.1 M KHCO$_3$, and a Sellemion AMV membrane with either an Al or graphite current collector. Based on these experiments, the Al current collector was chosen for the future because it captured a higher current efficiency (suggesting the cell sealed better) and resulted in more smooth i vs. t plots (the graphite current collector led to a higher current each time the GC sampled).

Another parameter that turned out to have a large effect on activity was the amount of Cu loaded onto the GDE. To prepare electrodes with different amounts of Cu, electrodeposition was used and the amount of charge passed during Cu deposition varied to get higher and lower loadings. The activity of the different electrodes was measured with their dark side toward the electrolyte and flow rate of 26 sccm (5 sccm through counter electrode compartment, 20 sccm through working electrode side liquid compartment, and 1 sccm through the gas side of the working electrode). Figure 4.3.4
shows the current efficiency for the gas phase products measured with different Cu loadings. Hydrogen dominates as the product at low loading and the activity approaches that of Cu foil measured in the standard cell as the loading is increased. In between the two extremes of loading, the activity varies widely with different products dominating. In addition to changes in product selectivity as a function of Cu loading, changes were observed over the course of hour at constant potential when low loading were used (Figure 4.3.5). Ethylene and methane were the most sensitive to deactivation over time, while current efficiency for CO did not go down as much. The fact that this occurred only when low Cu loadings were used suggests that deactivation may take place due to a trace impurity. If such an impurity is present, higher loadings would not be as susceptible to deactivation because the increased number of active sites could not all be blocked.

Figure 4.3.5. Deactivation of CO₂RR throughout electrolysis in GDE cell with 0.1 M KHCO₃ electrolyte.

Electrolyte concentration also has a large effect on product distribution. Figure 4.3.6 shows the result of using different electrolyte concentrations with a Cu loading of 0.059 mg total and flow rate of 26 sccm (5 sccm counter electrode, 20 sccm working electrode liquid side, and 1 sccm working electrode gas side). The Cu loading was relatively low, so the product distribution does not match what would be expected based on the Cu foil results and is instead dominated by hydrogen. Increasing the concentration
of KHCO$_3$ causes the overall current to increase. The changes in current make it difficult to compare different concentrations on a current efficiency basis, so instead Figure 4.3.6 shows the coulombs of charge that went to making each product. As with Cu loading, different concentrations change the relative amount of the different CO$_2$ reduction products, demonstrating that the activity is very dependent on electrolyte.

![Figure 4.3.6. Effect of KHCO$_3$ electrolyte concentration on CO$_2$RR products on Cu in the GDE cell.](image)

With CO$_2$, the flow rate in the 3 different compartments was controlled by individual mass flow controllers and they can be varied independently. It was decided to use 5 sccm flow in the counter electrode compartment to lower the amount of total gas flowing through the cell and a 20 sccm flow rate in the working electrode compartment to match the flow at the working electrode in the standard cell. A range of rates were tested to determine the flow on the gas side of the GDE. Figure 4.3.7 shows that the flow rate does not have that large of effect, but current efficiencies were slightly larger at lower flow rates. A flow rate of 1 sccm or 0 sccm was used in future experiments.
Figure 4.3.7. Effect of CO$_2$ flow rate through working electrode gas compartment on CO$_2$RR current efficiency on a GDE containing Cu.

The side of the GDE facing the electrolyte also affected activity. In a fuel cell, the catalyst particles are deposited onto the dark side of the GDE and the dark side is pressed into the ion exchange membrane to achieve optimal activity. The GDE cell differs from a fuel cell; instead of the GDE pressing up against a membrane it is exposed to electrolyte solution. Differences between a fuel cell and GDE cell for gas reduction led to testing which side of the GDE should be exposed to the solution. GDE electrodes were prepared by dropcasting 5 mgs onto the dark side of the electrodes. For this test, CO was reduced instead of CO$_2$. The cell was assembled with either the dark or light side of the electrode toward the electrolyte and flow rates of 0 sccm CO in the working electrode gas side and 20 sccm CO in the working electrode liquid side were used and the counter electrode was purged with nitrogen (working electrode gas and liquid side headspaces were connected, counter electrode side gas did not flow to the GC). Figure 4.3.8 compares the product distribution of CO reduction in the two configurations. In the ‘fuel cell’-like configuration, with the dark side of the electrode toward the electrolyte, there is a much higher current density and higher current efficiency for HER. Facing the dark side of the electrode toward the gas side of the working electrode compartment led to higher current efficiencies of CO reduction products. The applied voltages in the experiments compared in Figure 4.3.8 are different due to the different
amount of current drawn. When the dark side of the electrode faced the electrolyte, it was not possible to get to a very negative voltage because the current was too high.

Figure 4.3.8. Comparison of CO reduction current efficiency with the dark or light side of a GDE containing Cu particles facing toward the 0.1 M KOH electrolyte.

The best experimental conditions for gas reduction were determined by reducing CO$_2$ with a bicarbonate electrolyte (or CO in KOH electrolyte). Al was found to be a good current collector, high Cu loading improved performance, a low gas flow rate in the working electrode gas side slightly increased current efficiency, and depositing catalyst material on the dark side of the GDE and facing the dark side toward the working electrode gas side improved the current efficiency for reduction products. Parameters were determined using CO$_2$ (or CO in the case of GDE side to face to the electrolyte), but applying this setup in the reduction of CO led to improvement in the measured activity, probably due to better mass transport of CO to the metal surface. Figure 4.3.9 compares the current efficiency of CO reduction with 0.1 M KOH in the standard and GDE cell setup. There is more than an order of magnitude improvement in current efficiency using the GDE cell. To summarize the conditions used for the CO reduction experiments in the GDE cell (Chapter 5), Cu impregnated GDEs were prepared by dropcasting 5 mg of Cu nanomaterial. The GDE cell (polycarbonate) was assembled using an anion exchange membrane (Fumasep membrane, pH 1-14 stability range, supplied by Fumatech) and 8
mL of 0.1 KOH (Sigma-Aldrich, 99.99% metals basis) electrolyte was put into the liquid compartment of the working electrode side of the cell and the counter electrode filled with a matching level of electrolyte. The head spaces of the gas and liquid working electrode compartments were connected and CO flowed through the liquid side at a rate of 20 sccm to purge the headspace and bring products of CO reduction to the GC. Nitrogen gas flowed through the counter electrode side of the cell. Before reaching the cell, the CO gas flowed through a Teflon tube submerged in an acetone/dry ice bath and through a bubbler filled with 0.1 M KOH in order to remove any metal carbonyl impurities. GC and NMR were used to quantify products as described in Chapter 2.

![Figure 4.3.9. Comparison of CO reduction in standard and GDE electrolysis cells with 0.1 M KOH electrolyte.](image)

**Figure 4.3.9.** Comparison of CO reduction in standard and GDE electrolysis cells with 0.1 M KOH electrolyte.

The GDE cell is an improvement over the standard cell for the reduction of CO, but the results are also very sensitive to a number of parameters tested above. This sensitivity makes it difficult to draw unassailable conclusions until all of these factors can be understood and controlled.

### 4.4 Electrolyte limitations due to ion exchange membrane

The custom electrochemical cell described in Chapter 2 is well suited for the quantification of minor CO$_2$RR products under the conditions described: constant CO$_2$
flow and 0.1 M KHCO₃ electrolyte. The system is not as well suited for the reduction of other reactants (CO) or the use of other electrolytes. The use of an ion exchange membrane leads to limitations in the electrolyte that can be used. The ion that carries charge through the membrane must be generated by the electrochemical reaction(s) occurring at one side of the membrane and used up by the electrochemical reaction(s) occurring on the other side. If this condition is not met, then ion concentration differences on the two sides of the membrane result, which can cause junction potentials that show up as large cell resistances. Changes in ion concentration also lead to large changes in pH as buffering electrolyte is depleted or increased.

**Figure 4.4.1. Electrolyte limitations due to ion exchange membrane use.**

Figure 4.4.1a shows the initial electrolyte concentration under standard CO₂RR activity experiments, the reactions that occur during the experiment, and that the final electrolyte concentrations are unchanged, because bicarbonate anions are the current carrier through the membrane and equilibrate with CO₂ on either side of the membrane,
effectively acting as a hydroxide shuttle so that the electrolyte concentration stays constant. Figure 4.4.1b shows the result of switching to CO reduction in a 0.1 M phosphate buffer. There are two anions present, phosphate and hydroxide, and both can travel through the membrane. The concentration of phosphate is significantly higher, so it is likely the majority current carrier. The result is that as the reduction of CO continues, more and more phosphate is transported to the counter electrode side of the cell and more and more hydroxide accumulates in the working electrode side. The transport of the electrolyte buffer from one side of the cell to the other leads to large changes in pH. Phosphate and bicarbonate electrolytes both have the same initial pH, however, it is only possible to maintain the initial pH under reactions conditions when using a bicarbonate buffer. The use of phosphate with an ion exchange membrane is not ideal because the pH and electrolyte concentration are constantly changing throughout the reaction.

![Graph showing change in cell voltage over time](image)

**Figure 4.4.2.** Junction potential results from electrolyte ion transport through a Nafion membrane (cation exchange) during CO₂ reduction in 0.1 M KHCO₃.

Besides pH changes, problems due to the formation of a junction potential across the membrane can result from different ion concentrations on either side of the membrane. Nafion (a cation exchange membrane) was initially used to carry out CO₂RR experiments in KHCO₃ electrolyte. Before the end of the hour long electrolysis, the cell resistance would increase until the compliance voltage of the potentiostat was reached and the experiment would stop. Figure 4.4.2a shows the change in cell voltage observed over time. This result can be explained by the transport of potassium through the
membrane, leading to differing concentrations on the counter and working electrode side. Figure 4.4.2b shows the junction potential that is calculated to occur as potassium is depleted on the counter electrode side and builds up in the working electrode compartment during CO$_2$RR. The junction potential leads to large resistance to the movement of current through the cell, causing the potentiostat to reach the maximum applied cell voltage.

<table>
<thead>
<tr>
<th>Reactant:</th>
<th>CO$_2$</th>
<th>CO</th>
</tr>
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<tbody>
<tr>
<td>Electrolyte</td>
<td>Membrane</td>
<td>Electrolyte</td>
</tr>
<tr>
<td>$\geq 0.1$ M acid</td>
<td>Cation</td>
<td>$\geq 0.1$ M acid</td>
</tr>
<tr>
<td>$\geq 0.1$ M bicarbonate</td>
<td>Anion</td>
<td>$\geq 0.1$ M hydroxide</td>
</tr>
</tbody>
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Table 4.4.1. Permissible electrolyte and ion exchange membrane combinations.

To avoid junction potentials and pH changes during electrolysis, only certain combinations of electrolyte and ion exchange membranes can be used (Table 4.4.1). Bicarbonate is the only electrolyte that can be used at neutral pH, other electrolytes for CO$_2$ reduction are limited to those with a pH of $<1$. The use of high pH hydroxide as electrolyte is not possible because it will convert to bicarbonate in the presence of CO$_2$. Changing the reactant to CO (or another compound that does not react with the OH$^-$ or H$_2$O as CO$_2$ does), causes the choice of electrolyte to be limited to those with a pH of $<1$ or $>13$. The neutral pH that is possible with CO$_2$ is not possible with CO, because CO does not react with water or hydroxide to generate an ion that can travel through the membrane. The only electrolyte species that are present to go through the membrane are part of the buffer, which leads to junction potentials and pH changes. CO or CO$_2$ reduction can be done without using an ion exchange membrane, but contamination from the counter electrode can result (Section 5.5) and product identification (especially in the liquid phase) is less sure, because it is possible for reduction products formed at the cathode to travel to the anode and undergo partial oxidation. Restrictions on the pH of the electrolyte make it difficult to determine how pH affects CO$_2$RR.
4.5 References


Chapter 5. CO electroreduction

5.1 Abstract
To explore whether CO is a probable intermediate in the reduction of CO\(_2\) to the products of CO\(_2\)RR with a Cu electrode as described in Chapter 3, CO was electrochemically reduced and the products detected were similar to those of CO\(_2\)RR. Differences in the product distribution may result from differences in the electrode surface morphology, electrolyte composition, and pH. These effects are discussed and the results of CO and CO\(_2\) reduction are compared to other studies that have appeared in literature.

5.2 Introduction
CO is thought to be an intermediate on the reaction pathway from CO\(_2\) to hydrocarbons and alcohols on Cu metal. For this reason, the electroreduction of CO has also been studied, in order to eliminate the effect of the initial CO\(_2\) reduction step, which some authors believe to be rate limiting. Unlike CO\(_2\), CO does not react with aqueous soln and is not part of the electrolyte buffer. This may allow for better pH control, but it also means that the concentration of CO is only what will dissolve in the aqueous phase (approximately 1 mM). Comparing the results of CO\(_2\) and CO reduction is complicated by necessary differences in experimental conditions between the two reactions. Differences in bulk electrolyte concentration and mass transport can result in changes to product selectivity and reaction rate. At neutral and basic pH, different electrolytes must be used for CO and CO\(_2\) and electrolyte composition is known to influence the outcome of the reaction. In addition, it is not straightforward to run CO and CO\(_2\) reduction at the same pH. CO\(_2\) reacts with hydroxide to form bicarbonate, which lowers the pH and if an ion exchange membrane is used, a neutral pH is difficult to maintain during CO reduction due to transport of the buffer ions through the membrane (see Section 4.4).

For CO reduction, the GDE electrolysis cell described in Chapter 4 was used and the results will be compared to the results of CO\(_2\)RR on Cu in the standard electrolysis cell described in Chapter 2. Key differences between the conditions of CO and CO\(_2\) reduction are: electrolyte composition (0.1 M KHCO\(_3\) for CO\(_2\), electrolyte pH (pH 6.8 for CO\(_2\) and pH 13 for CO), and the electrode morphology (electropolished Cu foil for CO\(_2\).
and a GDE dropcast with Cu particles for CO). Understanding how each of these factors influences the results of the reaction is necessary to compare CO and CO\(_2\) reduction experiments and will ultimately be important to controlling the product selectivity and increasing the energy efficiency of the reaction.

The effect of electrolyte composition has been reviewed.\(^1\) When bicarbonate salts with different cations are used as the electrolyte with a Cu electrode, the trend is that larger cations favor ethylene production, while smaller cations favor methane. The effect of cation size has also been looked at with a Ag metal catalyst, and larger cations were found to favor CO\(_2\)RR (to CO), while smaller cations led to more HER current.\(^2\) Changes in activity with ion size are not understood, but ions are known to influence a number of important factors; they can adsorb to the electrode surface, stabilize charged intermediates, and change the potential of the double layer. The size of an ion determines its hydration number, which in turn changes the ability of the ion to interact in the ways listed. The effect of anions is more difficult to figure out, because anions also play a role in buffering the pH, so comparing different anions is not straightforward, but the strong correlation between cation size and activity suggests that changing the electrolyte anion could also change selectivity and efficiency of the reaction.

It has been reported that changes in pH can also influence CO\(_2\)RR activity. Higher pH favors ethylene production and neutral pH favors methane.\(^1\) Few studies have looked in the low pH regime, perhaps because HER is favored. Changes in pH have been achieved by changing the electrolyte buffer, but experimentally this can lead to a number of problems (see Section 4.4) because of the ion exchange membrane. Without an ion exchange membrane, contamination of the working electrode by metal from the counter electrode can occur. Lower electrolyte concentration favors ethylene production and higher electrolyte concentration favors methane.\(^3\) This could be an ion effect, but it is likely linked to changes in the electrode surface pH due to higher or lower electrolyte buffering ability with changes in concentration. CO\(_2\)RR uses up protons near the electrode interface and produces hydroxide, which increases the pH at the electrode surface. A strongly buffering electrolyte (higher concentration) can control the surface pH and keep it near the bulk electrolyte pH, but as the current density increases, eventually the surface pH will also increase.\(^4\) The bulk electrolyte pH is easy to
measure, but actual pH at the electrode surface is very difficult to know, which can make understanding the effect of pH difficult.

Another factor that can change activity is the electrode surface morphology. Cu single crystal and nanostructured surfaces have been studied. Exposed Cu(100) facets favor the formation of ethylene with a low overpotential and Cu(111) favor methane production, but a higher overpotential is needed. While these experiments use single crystal electrodes, the actual surface morphology during CO₂RR is not known. Cu forms a thin layer of oxide on exposure to air and aqueous electrolyte. The reduction of this oxide likely occurs before the onset potential of CO₂RR, and could lead to a different morphology than a perfect single crystal surface. Deliberate roughening of the Cu surface also leads to an increase in the ratio of ethylene:methane. Most nanostructured Cu electrodes have not been reported to possess an earlier onset potential or greater turnover frequency when the increased surface area is taken into account, but Kanan et al. have reported increased current efficiency and decreased overpotential for CO and formate production using a nanowire electrode and this is discussed more fully in Section 5.6.

Table 5.2.1 summarizes the effects which favor ethylene or methane production. One difficulty is determining if these factors are independent of one another or whether they are interconnected. For example, high pH and rougher electrode surface both lead to more ethylene. But these two conditions are not necessarily independent. At high pH, a thicker copper oxide may form, which is reduced during CO₂RR to a rougher metallic surface; the increase in ethylene may be due only to the surface roughening that results from high pH. On the other hand, it could be the reverse, a larger surface area leads to

<table>
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<tr>
<th>Favors</th>
<th>Ethylene</th>
<th>Methane</th>
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<tbody>
<tr>
<td>large cations</td>
<td>Cu(100)</td>
<td>small cations</td>
</tr>
<tr>
<td>rough surface</td>
<td>Cu(111)</td>
<td>electropolished surface</td>
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<td>neutral pH</td>
<td>high electrolyte conc.</td>
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<tr>
<td>low electrolyte conc.</td>
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Table 5.2.1. Factors that favor ethylene or methane formation.
higher current and therefore higher surface pHs at lower overpotential, so high pH could be the governing effect on increased ethylene observed when a rougher electrode is used.

This chapter discusses the results of CO reduction on Cu and a variety of experiments with different electrolytes, pHs, and electrode surface morphologies in order to better understand these effects and allow for comparison between CO and CO$_2$ reduction experiments. Results of these experiments largely agree with Table 5.2.1, but further study is needed to deconvolute the effects of the many experimental factors that influence activity.

5.3 Experimental Method

Briefly, CO reduction experiments run in the GDE electrolysis cell described in Section 5.4 used Cu impregnated GDEs prepared by dropcasting 5 mg of Cu nanomaterial as the working electrode. The GDE cell (polycarbonate) was assembled using an anion exchange membrane (Fumasep membrane, pH 1-14 stability range, supplied by Fumatech) and 8 mL of 0.1 KOH (Sigma-Aldrich, 99.99% metals basis) electrolyte was put into the liquid compartment of the working electrode side of the cell and the counter electrode filled with a matching level of electrolyte. The head spaces of the gas and liquid working electrode compartments were connected and CO flowed through the liquid side at a rate of 20 sccm to purge the headspace and bring products of CO reduction to the GC. Nitrogen gas flowed through the counter electrode side of the cell. Before reaching the cell, the CO gas flowed through a Teflon tube submerged in an acetone/dry ice bath and through a bubbler filled with 0.1 M KOH in order to remove any metal carbonyl impurities. GC and NMR were used to quantify products as described in Chapter 2.

CO reduction experiments in 0.1 M potassium phosphate electrolyte (Figure 5.4.7) were run with few modifications to the setup described in Chapter 2. The 0.1 M potassium phosphate buffer was made by preparing a soln of 0.5 M K$_2$HPO$_4$ and 0.5 M KH$_2$PO$_4$ (Sigma-Aldrich, 99.99% metals basis). The standard electrolysis cell was setup without an ion exchange membrane and the counter electrode gas inlets plugged. CO flowed at a rate of 20 sccm through through a Teflon tube submerged in an acetone/dry ice bath and through a bubbler filled with 0.1 M KOH in order to remove any metal
carbonyl impurities and then entered the cell through the bottom gas inlet of the working electrode side. CO exited through the top of the cell and was piped to the GC where aliquots of the gas were measured to get the composition at the regular time intervals.

CO$_2$ reduction experiments in 0.5 M KHCO$_3$ were done with the method described in Chapter 2 with the exception that the electrolyte concentration was higher and IR compensation was not used because the IR drop through the soln was <2 Ohms.

### 5.4 CO reduction

![Graph](image)

Figure 5.4.1. CO reduction current vs. time with Cu dropcast on a GDE in 0.1 M KOH electrolyte (pH 13).

The GDE cell with the experimental parameters given in Section 5.3 was used to reduce CO. Figure 5.4.1 shows the current drawn during CO reduction at each potential. Over the course of the hour at constant potential, the current increased steadily. It is hypothesized that the current increase comes about because the pores of the GDE fill with electrolyte to a greater extent as time passes. Before electrolysis, the gas side of the GDE appears dry, but after an hour, it is possible to see droplets of water forming on the gas side of the GDE, suggesting that the electrolyte has been slowly moving through the pores from the liquid side. The current increases as more surface area is exposed to electrolyte.
Figure 5.4.2 shows the partial current and current efficiency for CO reduction products. The current is not converted to a per area basis because the catalyst area is unknown. The geometric area of the GDE exposed to the electrolyte was 5 cm$^2$. Large differences can be seen compared to CO$_2$RR with Cu foil in the standard cell. Figure 5.4.3 compares CO$_2$ and CO reduction selectivity for products with a current efficiency over 10%. The fraction of the partial current density of each product to the total CO or CO$_2$ reduction current is plotted, with open symbols for CO$_2$ and solid symbols for CO. Both CO and CO$_2$ reduction result in ethylene as the majority product at low overpotential, but the selectivity for methane is very different. CO$_2$ reduction results in an increased amount of methane formed as the overpotential increases, but only a small portion of CO is reduced to methane. Instead, acetate is the second highest product.
formed when CO is reduced, but acetate is only a minor product of CO₂ reduction. Ethanol and n-propanol account for similar fractions of the products formed from CO or CO₂.

Figure 5.4.3. Comparison of CO and CO₂ reduction product selectivity on a GDE in 0.1 M KOH electrolyte (pH 13).

Differences in product selectivity are likely not the result of only the starting reactant. Many factors are different between the two experiments. The catalyst surface is rougher in the case of CO reduction vs. CO₂, which is believed to favor ethylene. For CO reduction, 0.1 M KOH (pH 13) was the electrolyte, vs. 0.1 M KHCO₃ (pH 6.8) for CO₂ reduction and high pH has also been suggested to favor ethylene formation over methane. The electrolyte composition (hydroxide vs. bicarbonate) is also different in the two cases and the reaction has been shown to be very sensitive to electrolyte composition. Mass transport is also likely to be different, which may affect selectivity, especially between single and multi-carbon products.
Although many factors are different between the CO and CO₂ reduction experiments, it is still possible to draw some conclusions. Previous studies have identified CO as a likely intermediate in CO₂ reduction to methane and ethylene because methane and ethylene also result from the reduction of CO. Many previously unreported products of CO₂RR were identified in Chapter 3 and it is important to determine if CO is an intermediate in their formation as well. Figure 5.4.4 shows the products of CO₂ reduction organized by number of electrons needed to form each product (from CO₂) along the x-axis and the number of carbons in each product on the y-axis. Products that are also formed from CO reduction are shown in red. Six products arise from CO₂RR that were not detected after CO reduction. Four of these are aldehydes, which may be products of CO reduction, but are not detectable because they are unstable at pH 13. In base, aldehydes undergo aldol reaction and condensation, which results in their polymerization.¹⁰ The other two expected products, that are not observed when CO is reduced, are hydroxyacetone and acetone, which are minor products of CO₂RR, so may be present below the detection limit of NMR after CO reduction.
Figure 5.4.5. Current and product onset potential for CO and CO\textsubscript{2} reduction on an RHE and SHE voltage scale.

Another major difference between CO and CO\textsubscript{2} reduction is the onset potential. Figure 5.4.5 compares the CVs of CO\textsubscript{2} purged 0.1 M KHCO\textsubscript{3} and CO purged 0.1 KOH and the partial current density of ethylene and methane. CO in KOH has a much earlier current onset in both the case of a Cu foil electrode in the standard cell and in the case of Cu particles in the GDE cell on an RHE voltage scale. Just as the current onset is earlier, the onset of ethylene and methane formation is also earlier when CO in KOH is reduced. There are many possible reasons for this, making it difficult to determine what is responsible for the earlier onset of CO reduction compared to CO\textsubscript{2} reduction. Section 5.6 discusses the possibility that the rate limiting step in ethylene formation does not involve a proton transfer, only an electron transfer, whereby the SHE scale might be more appropriate than the RHE scale for comparing CO\textsubscript{2} and CO reduction results.
One possible reason for the differences in onset is the difference in the Cu surfaces used to reduce CO and CO$_2$. The Cu particles used in CO reduction are rougher than the Cu foil surface used to reduce CO$_2$ in Chapter 3, so a larger number of active sites due to increased surface roughness may be the reason for a higher CO reduction activity. Although they are not exactly the same Cu surface, Figure 5.4.6 compares the results of CO$_2$RR in 0.1 M KHCO$_3$ on electrodeposited Cu on the GDE to the results of CO reduction in 0.1 M KOH on dropcast nanoparticles on the GDE. The products formed are similar, but none of the aldehydes were detected in the case of CO reduction, probably due to their instability at high pH, and acetate has a much higher current efficiency in CO reduction in KOH than in CO$_2$ reduction in KHCO$_3$. 

Figure 5.4.6. Comparison of CO (0.1 M KOH) and CO$_2$ (0.1 M KHCO$_3$) reduction products in GDE cell.
Another possibility is that CO₂ (and CO) reduction is favored at higher pH, but because the reaction between CO₂ and hydroxide lower the pH of an aqueous solution, it is not possible to test CO₂ reduction at pH 13 where CO reduction was run. CO reduction can be run at neutral pH, but the use of buffer electrolyte means that an ion exchange membrane cannot be used to separate the sides of the cell without changes to the electrolyte composition on either side of the membrane over time. Figure 5.4.7 shows the results of CO reduction in a 0.1 M phosphate buffer (pH 6.8) using a Cu foil electrode in the standard cell setup. Partial current density of CO reduction products is much lower than CO₂ reduction (presumably due to mass transport), but the onset potential for ethylene is the same as observed in CO₂RR and the onset of methane is only a little later. This suggests that at pH 7, CO and CO₂ reduction have similar onset potentials. These results could mean that CO/CO₂ reduction is favored at higher pH. However, it is not possible to directly measure the actual surface pH of the electrode when the reaction is occurring. In the case of experiments run at pH 7, it may also be possible that enough protons are used up and hydroxide generated in the electrochemical reduction, that the pH at the electrode surface increases, and is the same in the case of CO in KOH and CO₂ in KHCO₃ even though the pHs of the bulk electrolyte are different. Assuming the surface
pH to be the same as bulk would cause errors in the true overpotential when the voltages were shifted to an RHE scale.

Yet another possibility is that the onset potential of the reaction does not rely on the pH, but is instead constant on the Ag/AgCl (or SHE) scale. This would be the case if the rate determining step in the reduction of CO did not involve protons. This idea has been presented earlier for CO reduction to ethylene\(^3\) and will be discussed further in Section 5.6.

It is also possible that the initial reduction of \(\text{CO}_2\) to CO is the rate limiting step in the formation of methane and ethylene. The reduction of CO may be kinetically less difficult, so it occurs at a lower overpotential than \(\text{CO}_2\) reduction. This suggests that if a good catalyst for the reduction of \(\text{CO}_2\) to CO could be found (ie. Au, see Chapter 6), then it might be possible to use Cu to reduce the resulting CO to hydrocarbons at a lower overall overpotential than could be accomplished with Cu alone acting as the catalyst.

The high concentration of CO during CO reduction, as opposed to \(\text{CO}_2\) reduction, may also play a role in the earlier onset of hydrocarbon formation. Since the rate of CO reduction depends on the amount of CO available, it is possible that when \(\text{CO}_2\) is reduced to CO, the concentration of CO is initially too low for CO reduction to proceed forward at a reasonable rate. The higher overpotential necessary for \(\text{CO}_2\) reduction may arise from the need to generate enough CO to make further reduction favorable. By the same argument, CO reduction in phosphate buffer could have a later onset because of the low concentration of dissolved CO in aqueous solution. Improved mass transport with the GDE cell may contribute to the lower overpotential observed in Figure 5.4.5.

Beyond differences in pH, the makeup of the electrolyte also affects the product distribution. Most studies in this area have looked at the effect of varying the cation, but it is not unreasonable to think that differences in electrolyte anion would also lead to activity changes. One known difference between anions is their ability to interact with the surface and block sites until the electrode is brought to a low enough potential to cause anions to desorb. In the case of the CO reduction results presented, phosphate and hydroxide were the only anions present. In the case of \(\text{CO}_2\) reduction, bicarbonate, carbonate and hydroxide are the anions in solution. Phosphate and bicarbonate may interact more strongly with the Cu surface and desorb at a lower voltage than hydroxide.
The result of sites being blocked by adsorbed anions would be a later onset potential for the reduction of CO or CO$_2$.

Surface roughness, pH, reactant concentration, and the electrolyte composition are all factors that can affect CO$_2$RR (and CORR) activity. Unfortunately, it is difficult to deconvolute these effects to determine the principle reasons for the earlier onset potential of CO reduction shown in Figure 5.4.5. More work is needed in this area, as understanding these effects is important to controlling product selectivity and onset potential.

**5.5 Electrolyte effects**

Figure 5.5.1. CO$_2$RR results in 0.5 M KHCO$_3$ electrolyte on Cu foil in standard electrolysis cell setup.
Potassium bicarbonate electrolyte with a concentration of 0.1 M was chosen as the electrolyte for the majority of CO₂RR experiments because it was used in previous literature reports. Bicarbonate is the only electrolyte with a neutral pH that can be used with an ion exchange membrane, so it is a natural choice. Increasing the concentration to 0.5 M seems advantageous because it decreases the solution resistance to < 2 Ohms, which is low enough that IR compensation is not necessary to get an accurate voltage. But changing the concentration of KHCO₃ profoundly influences the product distribution. Figure 5.5.1 shows the current efficiency and partial current density of CO₂RR products in 0.5 M KHCO₃ from experiments run in the standard electrochemical cell as discussed in Chapter 2.

Figure 5.5.2. Comparison of CO₂RR product selectivity with 0.1 and 0.5 M KHCO₃.

Compared to the same experiments run in 0.1 M KHCO₃, the higher concentration electrolyte strongly favors HER at the expense of CO₂RR. Within the CO₂RR products there is also a change in the relative amounts of each. Many of the products observed in the case of the 0.1 M electrolyte are not detected at all. Amongst the products that are seen, major differences are the earlier onset and higher current density for methane as opposed to ethylene and the preference for ethanol production over ethylene in the case of 0.5 M electrolyte. Figure 5.5.2 shows the fraction of CO₂RR current going to make products in high and low electrolyte concentration at -1 V.

It is not obvious why increasing the electrolyte concentration should decrease the CO₂RR current. One possibility is that impurities in the electrolyte play a role. Using
0.1 M KHCO$_3$, no metal impurities were detected on the Cu electrode after electrolysis by XPS, but increasing the electrolyte concentration by 5x also adds 5x impurities, which may deposit on the Cu, blocking active sites and decreasing activity.

Increasing electrolyte concentration also increases the strength of the buffer, allowing for a higher current density before the surface pH begins to shift higher. A lower surface pH could be responsible for the differences in product distribution observed using 0.5 M KHCO$_3$. The CO reduction results at pH 13 in Figure 5.4.5 indicate that ethylene could be favored at high pH and methane is the favored product in lower pH phosphate electrolyte (pH 6.8), shown in Figure 5.4.7.

![Graph showing CO$_2$RR results](image)

Figure 5.5.3. CO$_2$RR results in 0.1 M potassium phosphate electrolyte on Cu foil in standard electrolysis cell with no ion exchange membrane.
The bicarbonate/CO₂ buffer is known to have relatively poor buffering ability compared to other buffers. This likely leads to poor control over the electrode surface pH when using bicarbonate electrolyte, especially at the lower concentration of 0.1 M. For this reason (and for comparison to CO which cannot be reduced in bicarbonate electrolyte without shifts in pH), CO₂RR was also carried out in 0.1 M potassium phosphate buffer (Figure 5.5.3). The current efficiency for CO₂RR is not as high in 0.1 M potassium phosphate as with 0.1 M KHCO₃ electrolyte, possibly because a lower concentration of bicarbonate in the electrolyte leads to lower mass transport (although the reaction does not appear to hit any diffusion limitations), but also possibly because the pH at the electrode surface is lower due to better buffering, which may favor HER. As with 0.5 M KHCO₃, many of the minor products detected in 0.1 M KHCO₃ are not seen. Ethylene and methane are the dominant products, but unlike with 0.1 M bicarbonate electrolyte, methane is favored over ethylene at all potentials and has an earlier onset. The onset potentials for CO₂RR in phosphate are close to those of CO reduction in phosphate electrolyte.

A complicating factor in interpreting the results is that an ion exchange membrane cannot be used to separate the working and counter electrodes (without changes to the electrolyte composition). This could lead to the oxidation of some CO₂RR products back to CO₂ at the counter electrode. Another problem is the possibility of anodic dissolution of Pt from the counter electrode and redeposition onto the Cu surface, which is prevented when an anion exchange membrane is used because the Pt cations dissolved in solution cannot cross the membrane. Pt deposition is likely the cause of changes in the gas phase product distribution measured later in the hour-long electrolysis when no ion exchange membrane is used (the same change in product distribution are not observed with an ion exchange membrane in place).
Figure 5.5.4. Change in gas phase product distribution over the hour electrolysis in the standard cell with a Cu foil electrode and 0.1 M potassium phosphate buffer. No ion exchange membrane was used, which allows for Pt from the counter electrode to contaminate the Cu working electrode and is likely responsible for ethane formation.

Figure 5.5.4 shows that after 5 mins the current efficiency for methane and ethylene is around 25% and 10% respectively for CO$_2$RR in potassium phosphate electrolyte, but the current efficiencies decrease upon successive measurements to less than 5% at the end of the hour. This deactivation is likely caused by Pt depositing onto the Cu electrode, which can occur because an anion exchange membrane does not separate the counter and working electrode sides of the cell in this experiment. Another change from the previously measured activity of Cu is the presence of ethane, probably
coming from the further reduction of ethylene. Ethane appears only at the most negative voltages tested and only after some electrolysis time. Ethane is probably also the result of Pt contamination of the Cu. Pt would be expected to bind ethylene more tightly than Cu, allowing the ethylene to be further reduced to ethane, instead of released as ethylene as in the case of pure Cu. Figure 5.5.5 shows the activity for CO$_2$RR measured at 5 mins, which is likely the measurement least contaminated with Pt. The current efficiency for CO$_2$RR is slightly higher at the most negative voltages than is shown in Figure 5.5.4 and there is no ethane detected. The data are noisier because fewer time points are averaged over.

Figure 5.5.5. Initial CO$_2$RR activity in 0.1 M potassium phosphate when less Pt contamination due to the lack of anion exchange membrane has occurred.
While there are other factors that could explain the data, it appears that higher pH favors ethylene formation and lower pH favors methane. The standard electrolyte choice, 0.1 M KHCO$_3$, promotes higher CO$_2$RR activity than either 0.5 M KHCO$_3$ or 0.1 M potassium phosphate when used with a Cu electrode.

5.6 Comparison to literature reports
The data collected on the activity of Cu for CO$_2$RR in the standard electrochemical setup agrees well with previous reports from Hori et al.$^{11}$ (Section 2.11). The same researchers have also studied the reduction of CO.$^3$ The key conclusion of their work is that the formation rate (partial current) of ethylene does not depend on pH, but the rate of methane formation does. This conclusion comes from CO reduction data collected in electrolytes with pHs ranging from 6-12. Some key experimental details are not given; the pH of different experiments is listed only as a range, so it is unclear whether the pH changed over the course of the experiment or whether the pH was slightly different between the experiments. The authors report that potassium phosphate or borate were used to buffer at different pHs, but they also used a cation exchange membrane to separate the working and counter electrodes. It is likely the pH shifted during CO electrolysis due to movement of potassium through the membrane (this may be why only a pH range is reported for different groups of experiments). It is also unclear whether the voltage or current was controlled in the reduction of CO. Performing the experiments at constant current and averaging the voltage could also lead to errors in the exact voltage value. Using the voltage (vs. SHE), partial current density, and average pH that they report, their data was converted to the RHE scale for comparison.
Figure 5.6.1. CO reduction results compared to data from Hori et al.³

Figure 5.6.1 shows data from Hori et al.³ on the same plot with CO reduction data from Figure 5.4.2 on an RHE and SHE reference scale. Plotted on an RHE scale, the methane data collected by Hori et al. has a similar tafel slope as the data collected in KOH and phosphate data points (before reaching a possible diffusion limitation). Hori’s methane data shows a trend toward increasing partial current with potential on an RHE scale, but his ethylene data does not display a strong trend (or there may be a slight trend toward decreasing partial current on the RHE scale). However, when plotted on an SHE scale, the ethylene data does have the expected trend of increasing partial current with potential. And on an SHE scale, ethylene data from Hori et al. and the Jaramillo lab agree fairly well.

While more data would be needed to confirm the pH dependence of methane formation and pH independence of ethylene formation described by Hori, data collected in the Jaramillo lab does not conflict with Hori et al.’s conclusions. Data collected in the two laboratories show similar tafel slopes and onset potentials for methane and ethylene on RHE and SHE voltage scales respectively. The dependence of methane formation rate on pH is expected, since protons are needed for the reduction of CO. The pH independence of ethylene formation is difficult to understand. Protons are also needed for the reduction of CO to ethylene, but pH independence indicates protons are not involved in the rate determining step. One key difference between methane and ethylene...
formation is the need for a C-C coupling step to form ethylene. C-C coupling could be an electrochemical or a purely chemical step. In either case it is conceivable that C-C coupling could be independent of pH. An electron transfer independent of a proton transfer could be needed to form the C-C bond in an electrochemical C-C coupling step. If the step is chemical, then it would depend directly on the coverage of $C_1$ intermediates that can undergo coupling and only indirectly on potential and pH. Understanding and controlling C-C coupling is important to controlling the product selectivity. Favoring C-C coupling could be a way to form longer chain hydrocarbon products and energy dense liquid fuels.

Figure 5.6.2. CO$_2$RR results in 0.5 KHCO$_3$ compared to Kanan et al.$^8$

More recent work to understand Cu activity has also appeared in the literature. Kanan et al.$^8$ reported that they were able to improve the onset potential and current efficiency for CO$_2$RR to form CO and formate using a nanostructured Cu electrode compared to the results of Hori et al.$^{11}$ using a flat electrode. While Kanan et al. do see higher activity for CO and formate, they see much lower activity for hydrocarbons and alcohols. A likely reason for this is that they used 0.5 M KHCO$_3$ as the electrolyte instead of 0.1 M KHCO$_3$ used by Hori et al. A more fair comparison to determine the effect of nanostructuring compared to a flat Cu electrode would be to compare data
collected in the same concentration electrolyte. Figure 5.6.2 shows data reported by Kanan et al. compared to the activity of a flat Cu electrode reported in Figure 5.5.1. The current density on the flat and nanostructured electrodes are quite similar. This is unexpected due to the much higher surface area of the nanostructured electrode, but could possibly be explained by the change in product distribution between the two electrodes. The flat electrode has very low current efficiency for CO₂RR and instead favors HER. Nanostructuring increases the current efficiency of CO₂RR. Since CO₂RR is kinetically more difficult (slower) than HER, this could explain the lower than expected current on the nanostructured electrode. CO₂RR also has an earlier onset potential on the nanostructured electrode. This is likely due to the nanostructured surface binding more strongly to the initial CO₂RR intermediate. The first proton electron transfer in CO₂RR is believed to be the rate determining step on the pathway to CO and formate. Binding the first intermediate in CO₂RR more tightly would decrease the onset potential for the reaction. In 0.5 M KHCO₃, both the nanostructured and flat Cu surface show very low current efficiency for hydrocarbons, but there are difference in the hydrocarbon products observed. Methane is favored on the flat Cu surface. The nanostructured surface favors the production of ethylene and ethane. This shift in product selectivity towards ethylene and ethane is consistent with what has been reported by other labs for roughened Cu surfaces, but the increase in current efficiency for CO and formate has not been discussed in other publications. It is not clear if an increase in CO and formate relative to HER is unique to the specific nanostructures generate by Kanan et al., or if it is the result of combining a nanostructured surface with a higher concentration electrolyte which leads to better buffering and a lower surface pH. More studies to understand the interplay of pH and surface morphology would be interesting.
Koper et al.\textsuperscript{12} have recently reported on the CO reduction activity of Cu using a differential electrochemical mass spectrometer (DEMS) to measure products. With the DEMS it was not possible to determine current efficiency, but the mass spectrometer ion current for methane and ethylene is given, which shows the onset potential and relative formation rate of each product at pH 7 and pH 13 in sodium phosphate and sodium hydroxide electrolyte solns. Figure 5.6.3 plots their DEMS measurements with the CO reduction data presented in Section 5.4. The data from Koper et al. shows a much lower overpotential for ethylene, especially at pH 13. The data was collected while sweeping the potential; ethylene initially increases, but then decreases as the potential goes more negative and, on the return sweep, no ethylene is measured at potentials where it appeared during the negative-going sweep. Our data does not match the ethylene activity reported by Koper et al., but it roughly matches the methane activity they report. Discrepancies in ethylene activity could be related to the way the measurements were done. The electrolysis method is best suited to measuring stable, long term activity. The DEMS method is capable of measuring activity on a much shorter time scale.
Figure 5.6.4. Change in product distribution over time on Cu foil using standard electrolysis cell and 0.1 M KHCO$_3$ at low overpotentials.

Some measurements using the electrolysis method at low overpotentials suggest that there may be transient ethylene activity. The data in Figure 3.7.1 shows the current efficiency of CO$_2$RR on Cu, down to the lowest overpotential of -0.67 V vs. RHE. Activity at lower overpotentials was difficult to measure because it changed over the course of an hour-long electrolysis. Figure 5.6.4 shows the current efficiency for CO$_2$RR using a Cu electrode at -0.6 V vs RHE over the course of an hour. The measurement at 5 mins shows around a five percent current efficiency for ethylene, but no ethylene was measured at later time points. The current efficiency of methane and CO is also higher at 5 mins and decreases throughout the hour, although both products are still detected. The decrease in current efficiency for CO$_2$RR coincides with an increase in the total current. Figure 5.6.5 shows CVs taken before and after holding the potential at -0.6 V. The onset of both CVs is similar, but the slope is much higher after the experiment.
Figure 5.6.5. CV before and after CO$_2$ electrolysis at low overpotential.

In the standard electrolysis measurement procedure, a CV is taken before and after holding the potential constant for one hour. Unexpectedly, whether or not an initial CV is taken has an impact on the CO$_2$RR activity. Figure 5.6.6 shows the current during the hour at constant potential with and without an initial CV. When the CV is taken, the current increases throughout the hour (corresponding to an increase in the CV current shown in Figure 5.6.5). When no CV is taken, the current is flat over the course of the hour (except for an initial dip when the voltage is first applied). Without the initial CV, the CO$_2$RR activity was more consistent over the hour, but it was very low, less than 2%. In either case, using an electrolysis method, it is difficult to assess activity on a short time scale (ie. the first 5 mins after the constant potential is applied). Although it may require different tools than the electrolysis method, determining the cause of low overpotential CO$_2$RR activity is promising for the development of a more efficient process and will need to be looked into further.
Figure 5.6.6. CO$_2$RR current vs time with and without an initial CV.

5.7 References

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Chapter 6. Trends in transition metal activity

6.1 Abstract
The CO\textsubscript{2}RR activity of Au, Ag, Zn, Cu, Ni, Pt, and Fe was studied and compared. The activity follows a volcano relationship when plotted against CO binding strength. CO\textsubscript{2}RR mass transport limitations appear to affect the activity at high overpotential. The Tafel slope of HER and CO\textsubscript{2}RR are calculated and compared in the low and high overpotential regime. Due to the sensitivity of the experimental method used, a number of new products are observed. Methane or methanol or both are formed on all the metals studied and similar trends in partial current density for each lead to the conclusion that they arise from a shared mechanistic pathway. Ag, Ni, and Cu are the only metals to form multi-carbon products. The identity, potential dependence, and partial current density for the multi-carbon products are discussed. A better understanding of pure metal activity for CO\textsubscript{2}RR can hopefully guide the design of new catalysts by alloying or nanostructuring.

6.2 Introduction
The majority of CO\textsubscript{2}RR studies have focused on the transition metals.\textsuperscript{1-4} Hori et al. reported in 1985 that methane (CH\textsubscript{4}) and ethylene (C\textsubscript{2}H\textsubscript{4}) were the main products of CO\textsubscript{2}RR when Cu metal was used as a catalyst.\textsuperscript{5} A number of reports have compared the activity of different transition metals and found that the product yield and composition of CO\textsubscript{2}RR depend on the binding energy of CO, which is believed to be an important intermediate in the reduction of CO\textsubscript{2}, to the transition metal catalyst used.\textsuperscript{6} Metals that bind CO strongly produce few CO\textsubscript{2}RR products because they are poisoned by CO or other intermediates that form during CO\textsubscript{2}RR and consequently hydrogen from competing water reduction is the main product observed. On the other hand, metals that bind CO weakly produce mostly CO as a product, because when CO\textsubscript{2} is reduced to CO, the CO is released from the surface and does not go on to form more reduced products such as alcohols and hydrocarbons. Cu possess an intermediate binding energy for CO, which is
believed to be the reason for its unique ability to catalyze the formation of more reduced products that require more than a 2 electron reduction. \(^7\)

Chapter 2 outlines an experimental method for testing CO\(_2\) reduction catalyst activity with unprecedented sensitivity for the identification and quantification of CO\(_2\) electroreduction products. This method allowed for the discovery of five minor products of CO\(_2\)RR on Cu formed at high overpotential that had not been previously detected using other experimental methods.\(^8\) A full picture of the product distribution is paramount to gain understanding of the mechanism for CO\(_2\) reduction on the catalyst surface. The hunt for superior catalyst materials with higher CO\(_2\)RR activity by, e.g. alloying of transition metals, necessitates a deeper understanding of the elemental transition metal building blocks through a similar thorough investigation.

<table>
<thead>
<tr>
<th></th>
<th>CO $\rightarrow$ CO(^*)</th>
<th>$\frac{1}{2}$ O(_2) $\rightarrow$ O(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-0.07</td>
<td>Au 0.245</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.23</td>
<td>Ag -0.255</td>
</tr>
<tr>
<td>Au</td>
<td>-0.48</td>
<td>Pt -1.05</td>
</tr>
<tr>
<td>Cu</td>
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<td>Cu -1.45</td>
</tr>
<tr>
<td>Ni</td>
<td>-1.30</td>
<td>Ni -2.2</td>
</tr>
<tr>
<td>Pt</td>
<td>-1.30</td>
<td>Zn</td>
</tr>
<tr>
<td>Fe</td>
<td>-1.76</td>
<td>Fe -3.1</td>
</tr>
</tbody>
</table>

Table 6.2.1. Binding strength of CO\(^9\)-\(^{11}\) and O\(^{12}\) to each metal surface.

Six transition metals were studied, apart from copper. The metals selected were Au, Ag, and Zn, which bind CO weakly, and Ni, Pt, and Fe, which bind CO strongly (Table 6.2.1). It was possible to gather consistent data on each metal with complete characterization of the minor products formed and their potential dependence. Interestingly, methane and/or methanol were formed on all metals tested and the data collected suggest these two products follow similar mechanistic pathways and the step determining whether methane or methanol is formed occurs late in the reaction.

The activity of the metals studied follows a volcano relationship when plotted against the CO binding energy to the surface of each metal, indicating that the ideal strength for the metal surface to CO bond lies near that of Au and that formation of products requiring more than 2 electrons is likely to occur when the CO bond strength is
between that of Au and Cu. Better understanding of the mechanism of methane and methanol formation, the universality of hydrocarbon and alcohol formation, and the relationship of CO to surface bond strength to activity will help guide the design of improved CO$_2$RR catalysts.

6.3 Methods
Experimental methods used were outlined in Chapter 2. Briefly, using a custom electrochemical cell, electrolysis experiments were carried out in 0.1 M KHCO$_3$ electrolyte at constant voltage with IR-correction performed by the potentiostat. Gas chromatography was used to quantify the amount of gas phase products and NMR was used to quantify the concentration of liquid phase products. From the concentrations it was possible to calculate current efficiencies and partial current densities for each product. Three electrolysis experiments were run at each potential and the results averaged to give the data herein. The preparation of each type of metal electrode is given below.

**Cu.** Foil purchased from Alfa Aesar (1.0mm thick, product #42975, 99.999% metals basis). Before each electrolysis experiment, the foil was mechanically polished (400G sandpaper, 3M) and then electrochemically polished at 2.1 V vs. a graphite foil counter electrode in 85% H$_3$PO$_4$ followed by rinsing with 18.2 MΩ deionized water from a Millipore system.

**Ni.** Foil purchased from Alfa Aesar (0.1mm thick, product #12046, lot #B11X051 and G29U009, 99.994% metals basis). Before each electrolysis experiment, the foil was mechanically polished (400G sandpaper, 3M) and rinsed with 18.2 MΩ deionized water from a Millipore system.

**Fe.** Foil purchased from Alfa Aesar (0.1mm thick, product #40493, lot #B27U015, 99.99% metals basis). Before each electrolysis experiment, the foil was mechanically polished (400G sandpaper, 3M) and rinsed with 18.2 MΩ deionized water from a Millipore system.

**Pt.** Foil purchased from Alfa Aesar (0.05mm thick, product #42456, lot #J19R006, 99.99% metals basis). Before each electrolysis experiment, the foil was electrochemically cleaned by applying +4V vs. a Pt mesh in 30% nitric acid, rinsing with
18.2 MΩ deionized water from a Millipore system, and the PtO surface was potentiostatically reduced at -0.20 V vs. Ag/AgCl for 3 minutes in the electrolysis cell immediately prior to electrolysis.

**Zn.** Foil purchased from Alfa Aesar (1.0mm thick, product #11915, lot #J08S021, 99.9985% metals basis). Before each electrolysis experiment, the foil was mechanically polished (400G sandpaper, 3M) and rinsed with 18.2 MΩ deionized water from a Millipore system.

**Ag.** Foil purchased from Alfa Aesar (0.1mm thick, product #12126, lot #D22W016, 99.998% metals basis). Before each electrolysis experiment, the foil was mechanically polished (400G sandpaper, 3M) and rinsed with 18.2 MΩ deionized water from a Millipore system.

**Au.** Foil purchased from Alfa Aesar (0.1mm thick, product #11391, lot #C01Y014, 99.9975+% metals basis). Au foils were left overnight in concentrated nitric acid and rinsed with 18.2 MΩ deionized water from a Millipore system prior to each experiment.

### 6.4 CO₂ vs. H₂ Selectivity

For each metal studied, potentiostatic electrolysis experiments were run at a range of potentials and the average current density is shown in Figure 6.4.1a. The products of CO₂RR in the gas and liquid phase and the amount of hydrogen formed by competing water reduction were measured at each potential. Figure 6.4.1b shows the percentage of the total current at each potential that went towards CO₂RR instead of making hydrogen. This data confirms what has been reported previously. Au, Ag, and Zn which bind CO weakly, are good CO₂ reduction catalysts because they have a high current efficiency for CO₂ reduction, whereas Ni, Pt, and Fe, which bind CO strongly, are poor CO₂ reduction catalysts and mostly produce hydrogen. Cu, with a moderate CO binding energy, shows good current efficiency for CO₂RR, but less than Au, Ag, or Zn. The current efficiency for CO₂RR on Au, Ag, Zn, and Cu all decrease at the highest overpotentials measured. This is likely an effect of mass transport as will be discussed in the next section.
6.5 Mass transport limitations

Figure 6.5.1a shows the average CO$_2$RR current over the course of the hour at constant potential. The current on Au, Ag, and Zn levels out around -2.5 to 5 mA/cm$^2$. The current plateau is not flat in the case of these three metals. At the highest overpotentials measured there is a decrease in the absolute value of the current density. The maximum CO$_2$RR current is likely limited by mass transport. And the decrease in current at the highest overpotentials could be explained by a decrease in the amount of CO$_2$ reaching the electrode because hydrogen bubbles coming off of the surface remove CO$_2$ from solution before it reaches the surface. There could also be pH effects on the mass transport due to changes in the concentration of buffer ions, such as hydroxide, bicarbonate, and carbonate, that could affect the delivery of CO$_2$ to the surface.
In contrast to the other good CO$_2$RR catalysts, current on Cu continues to increase across the potential range. This can be explained by Figure 6.5.1b, which plots the total moles of CO$_2$ reduced over the course of an hour. Au, Ag, and Zn plateau around the same number of moles reduced, but fewer moles of CO$_2$ are reduced on Cu. The main product of CO$_2$RR on Au, Ag, and Zn is CO, a two electron product. On Cu, the main products are methane and ethylene, which require 8 and 12 electrons respectively. For Cu, more electrons are needed to reduce each molecule of CO$_2$, which results in a higher current density for CO$_2$RR than for metals that make mostly two electron products. Although Cu does not reach the CO$_2$ diffusion limit observed on other metals, the total moles of CO$_2$ reduced is near enough to the diffusion limit that mass transport likely does affect the reaction kinetics (tafel slope) and perhaps product selectivity (ethylene vs. methane). Design of an electrolysis cell with improved or better controlled mass transport is needed to separate the effects of mass transport from inherent catalyst activity.

![Figure 6.5.1](image-url)  
Figure 6.5.1. CO$_2$RR partial current density and moles of CO$_2$ reduced.

### 6.6 Tafel slope of CO$_2$RR and HER

Figure 6.6.1 is a Tafel plot of the HER current density during CO$_2$ electrolysis on the seven metals studied. For poor CO$_2$RR catalysts (Ni, Pt, and Fe), HER current appears as a straight line in the plot. For the good CO$_2$RR catalyst (Au, Ag, Zn, and Cu), HER appears to follow different trends at low and high overpotential. The dotted lines on the plot show fits to the data and the Tafel slopes derived from the fits are shown in the table.
to the right of the graph. All the listed HER Tafel slopes are higher than values traditionally reported in the absence of CO$_2$, which usually fall between 40-120 mV in acidic solution.$^{13}$ The Tafel slopes at low overpotential for Ag, Zn, and Cu are especially high. The low overpotential Tafel slope for Au was not calculated because all the datapoints are close to the region where CO$_2$RR reaches a diffusion limitation. The reason for the high Tafel slope at low overpotential is likely due to the concurrent reduction of CO$_2$ taking place on the metal surface, which inhibits HER. The Tafel slope decreases at higher overpotential where HER does not have to compete with as much CO$_2$RR because of diffusion limitations.

![Figure 6.6.1. Tafel plot and slopes of HER partial current density.](image)

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<td>Fe</td>
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</table>

$^a$Low overpotential
$^b$High overpotential

Figure 6.6.2 is a Tafel plot of the CO$_2$RR current. The plot clearly shows the CO$_2$ diffusion limitation at high overpotential. The dotted lines indicate fits to the data and the Tafel slopes of each line are given to the right of the graph. Again, the Au data is not fit because the data points are too near to the diffusion limited current density to get meaningful data. The Fe data is also not fit because it does not have a discernable potential dependence. The data for Cu was fit in the low and high overpotential regions, although both are relatively close in Tafel slope. Pt and Ni, both poor CO$_2$RR catalysts, have the lowest tafel slopes. Ag, Zn, and Cu all have relatively high Tafel slopes.
It would be very convenient if there were a quick electrochemical method to test whether a material showed activity for CO$_2$RR. A method that some researchers have attempted is to compare catalyst CVs taken in N$_2$ and CO$_2$ purged solutions and attribute differences in the current to CO$_2$ reduction.$^{14}$ Other researchers have stated that it is not possible to judge CO$_2$RR activity in this way.$^7$ Figure 6.6.3 shows the Tafel plot behavior of the total current density on each metal. Unfortunately, there is no clear way to differentiate the good and bad CO$_2$RR catalysts based on the Tafel slopes measured. Although Au, Ag, and Zn do have similar (and high) tafel slopes, Cu, which arguably makes the most interesting products has a similar Tafel slope to Pt, which has poor CO$_2$RR activity. Nor are there abrupt changes in Tafel slope across the potential range to differentiate regions where either CO$_2$RR or HER are the dominant reaction occurring at the electrode. Appendix I further discusses the difficulty in using only electrochemical methods to measure CO$_2$RR activity by comparing CVs of the metals studied in CO$_2$ purged and nitrogen purged solutions.
6.7 Minor products of CO\textsubscript{2}RR

The overall current efficiency and onset potentials for CO\textsubscript{2}RR show important activity trends for the transition metals studied, but a deeper understanding may be gained by looking in detail at the product distribution over the potential range. Using our method sensitive to minor product quantification, we found that Cu is not unique in the ability to catalyze hydrocarbon and alcohol formation. All of the metals tested in this study produced, either, methane, methanol, or both along with a few other previously unreported minor products. The highest quality and self-consistent data set regarding the activity of transition metals has come from Hori et al.\textsuperscript{7} Table 6.7.1 compares the data reported by Hori et al. to the data collected in this study at: i) a similar potential to the voltage reported by Hori et al., ii) a similar current density, and iii) the earliest potential where we observed the formation of hydrocarbons and alcohols on each metal.

The greatest difference compared to the data from Hori et al. is that we observe alcohol and/or hydrocarbon products with all the metal catalysts tested. While this can be partially explained by the sensitivity of our methods for minor product detection, in many cases, the potential where we first detected the formation of more reduced products was more negative than the potential explored by Hori et al. This highlights the importance of studying the activity of a given catalyst over a large potential range. Another notable
difference between the datasets is that Hori et al. used galvanostatic electrolysis to generate measurable products and report the average, IR-corrected potential of each experiment run at -5 mA/cm², while data present in this study was collected potentiostatically with IR-compensation and the current reported is the average current recorded at each potential. Performing the experiments potentiostatically has the advantage of offering better control over reaction kinetics. However, the use of IR-compensation does add some uncertainty to the voltage measurement, which is shown in Table 6.7.1.

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<th>C₂H₅</th>
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*a* Value includes additional contributions from n-propanol, allyl alcohol, acetaldehyde, and propionaldehyde  
*b* Value includes above and contributions from hydroxyacetone, acetone, ethylene glycol, and glycolaldehyde  
*c* Value includes contributions from ethane

Table 6.7.1. Comparison to CO₂RR data from Hori et al.

These results further show that a higher overpotential was needed to make the more reduced products, such as hydrocarbons and alcohols, compared to the overpotential needed to form two electron products, such as formate and CO. This is consistent with a recently proposed model,¹⁵ suggesting that on Cu and metals that bind CO more strongly, the initial two electron reduction of CO₂ to CO is kinetically easier than the step leading to the further reduction of CO, which requires a higher
overpotential. On metals that bind CO more weakly than Cu, CO desorption is believed to be faster than CO reduction.

One difficulty in the field of CO$_2$ reduction is the number of conflicting and irreproducible reports of catalyst activity. It has been suggested that contamination by trace carbon sources$^{16,17}$ or metal impurities$^{6,7}$ may be responsible. To rule out the possibility that liquid phase minor products observed in this study come from sources other than CO$_2$ reduction, $^{13}$C labeled CO$_2$ was reduced on each metal at a potential where novel minor products were observed and incorporation of the $^{13}$C label into the product confirmed by the peak splitting observed in $^1$H NMR. While it is more difficult to completely rule out trace metal impurities, Appendix D discusses the precautions taken to avoid them and the XPS spectra collected after electrolysis experiments, which showed no other metals present.

Figure 6.7.1. $^{13}$C incorporation into formate from $^{13}$CO$_2$ reduction.
6.8 Trends in methane and methanol formation

The products that all the metals tested had in common were methane and methanol. The only metals that did not make both of these products were Au and Fe, which produced only methanol and methane, respectively. Figure 6.8.1 shows the partial current density of methane and methanol across the potential range studied. Among the metals that make both products, methane and methanol appear at similar onset potentials. Deviations from this can be explained by a better detection limit for methane (10 \( \mu \text{A/cm}^2 \)) compared to methanol (50 \( \mu \text{A/cm}^2 \)). The fact that the formation of both products was catalyzed by most metals and that the partial current densities of each product track each other across the potential range suggests that the mechanistic pathway to methane and methanol share many common intermediates and that the two pathways are only differentiated late in the reaction. Since the final C-O bond must be broken to form methane but not in methanol, it follows that this C-O bond cleavage must occur late in the reaction pathway.
Figure 6.8.1. Methane and methanol partial current density.

Whether the C-O bond is cleaved or not to form either methane or methanol respectively could explain the product selectivity observed on Au and Fe. Formation of methane requires the C-O bond to be broken and the oxygen atom to bind to the surface to be later cleared as water. This pathway may be favored by the Fe surface with a strong binding affinity for oxygen (Table 6.2.1). The formation of methanol leaves the C-O bond intact and avoids a metal surface-oxygen bond. This pathway may be favored by Au because of the unfavorable surface-oxygen bond (Table 6.2.1). Fe and Au lie at the high and low end of oxygen binding energies, respectively; the oxygen binding energies of the other metal surfaces may not be extreme enough to influence kinetic factors in a straightforward way leading to only a single product.
6.9 Volcano plot

Figure 6.9.1 plots the CO$_2$RR activity data shown in Figures 6.4.1 against the binding energy of CO to each metal surface (Table 6.2.1). Figure 6.9.1a plots the partial current density for CO$_2$RR at -0.8 V vs. RHE. The activity (measured by the partial current density) does not linearly follow a trend with respect to the CO binding energy. Instead, it follows a volcano-type relationship, based on the Sabatier principle.$^{18}$ This principle states that there is an ideal binding energy for key intermediates that is neither too strong nor too weak. Au has the earliest onset and highest partial current density for CO$_2$RR, followed by Ag, then Cu and Zn. The high activity displayed by Au suggests that it has a CO binding energy nearer to the ideal value than any other pure metal. Ag and Zn form too weak of bonds to CO so they show lower activity for CO$_2$RR than Au. Cu has a stronger CO bond strength and catalyzes the formation of more reduced products with high current efficiency, however, it has lower overall activity than Au for CO$_2$RR. This suggests that there may be a CO binding strength between Au and Cu where more reduced products would be formed, but with an earlier onset and higher partial current density for CO$_2$RR than Cu.

Figure 6.9.1. Volcano plot of a) onset potential of HER, CO$_2$RR, and hydrocarbons and alcohols and b) partial current density for CO$_2$RR at -0.8V vs. CO binding strength.

Figure 6.9.1b is a plot of the onset potential for HER, CO$_2$RR, and the more reduced products methane and methanol, with dashed lines to guide the eye. Several
differences are apparent between the metals with good and bad CO$_2$RR activity. On the metals with good activity, the onset of HER and CO$_2$RR occurs at the same potential. On Ni, Fe, and Pt, which have poor activity, the onset of HER is considerably earlier than the higher overpotential needed to observe CO$_2$RR products. In the case of these metals, it is likely that CO$_2$RR occurs earlier or simultaneously with HER, but the product of CO$_2$RR is an adsorbate that poisons the metal surface for further CO$_2$ reduction. It is only at higher overpotential where the poisoning species is reduced further, to a product which is released from the surface and detected. The dashed red line is fitted to the HER onset potentials on the transition metals studied. There is a trend toward earlier HER onset voltage on metals that bind CO tightly.

Figure 6.9.1b further shows that the majority of metals have an earlier onset for CO$_2$RR to formate and CO than to methane and methanol (or other products requiring more than 2 electrons). Fe and Ni are exceptions due to detection of no 2 electron products (CO and formate) in the case of Fe and the only formate in the case of Ni, so the onset of CO$_2$RR on these metals coincides with the onset of methane/methanol. In the case of Fe and Ni it is believed that CO is still produced as an intermediate, but CO is not detected with our methods because it stays on the catalyst surface due to the strong surface-CO bond.$^{19-21}$ The higher overpotential needed to make the more reduced products, such as methane and methanol, compared to the overpotential needed to form two electron products, such as formate and CO is consistent with a recently proposed model,$^{15}$ suggesting that on Cu and metals that bind CO more strongly, the initial two electron reduction of CO$_2$ to CO is kinetically easier than the step leading to the further reduction of CO, which requires a higher overpotential.

The overall trend in CO$_2$RR activity is that metals that bind CO weakly have a higher current efficiency for CO$_2$RR than metals that bind CO tightly. However, the dashed blue line, fitted to the onset voltages of methane and methanol in Figure 6.9.1b, shows the reverse trend in onset potential of the more reduced products. Metals that have a strong CO binding energy (Ni, Pt, and Fe) have lower onset potentials for methane and methanol formation. Au, Ag and Zn, which have weak CO binding energies, show the highest overpotentials for methane and methanol formation. Cu, which has a high current efficiency for more reduced products, has an onset potential in between the metals that
bind CO strongly and those that bind CO weakly. The differences in onset potential for more reduced products could be explained by different coverages of CO or a similar intermediate. There is spectroscopic evidence to suggest that during CO$_2$ reduction the surface coverage of CO on Cu,$^{22,23}$ Ni,$^{19,20}$ Pt,$^{24}$ and Fe$^{20}$ catalyst surfaces is high. A high coverage of CO could compensate for a low rate constant for CO reduction to more reduced products in the case of Ni, Pt, and Fe. Au, Ag, and Zn, on the other hand, are expected to have very low surface coverages of CO, which would limit the formation of more reduced products, since CO desorbs before it can be further reduced. At the highest overpotentials tested on Au, Ag, and Zn, the rate of CO reduction may begin to compete with the rate of CO desorption, giving rise to small amounts of more reduced products.

6.10 Trends in multi-carbon product formation

Of the metals tested, only Cu, Ni, and Ag produced products with two or more carbons. Figure 6.10.1 shows the products of CO$_2$RR on each metal electrode. All three metals make nearly the same single carbon products. The exception is Ni, which does not make any observable CO, but CO has been detected on the surface of the electrode during CO$_2$RR. The multi-carbon products made by each of the metals are quite different. Ag makes only ethanol, an oxygenate. Cu makes a diverse mixture of hydrocarbons and oxygenates. Ni makes only hydrocarbons (ethylene and ethane). In Section 6.8, the selectivity of Fe and Au for methane and methanol was related to oxygen binding strength to the surface. Similar reasoning could explain the distribution of multi-carbon products. Of the multi-carbon product making metals, Ag forms the least favorable bond to oxygen, followed by a stronger oxygen bond to Cu and the strongest oxygen bond to Ni. A stronger bond to oxygen may favor C-O bond cleavage (Ni) and a weaker bond may favor leaving the C-O bond intact (Ag).
The formation of single vs. multi-carbon products appears to be potential dependent. Figure 6.10.2 shows the percent of CO$_2$RR current for more reduced products (those requiring >2 electrons) going to make multi-carbon products. On Cu, there is a clear trend favoring multi-carbon products (ethylene) over single carbon products (methane) at low overpotential. As the overpotential increases, single carbon products are favored. A similar trend holds for Ni. At low overpotential the percent of the current going to make multi-carbon products is ~42% and as the overpotential is increased it drops to <10%. The Ag data shows no clear trend; the percent of current producing multi-carbon products is fairly constant.

<table>
<thead>
<tr>
<th># of e(^{-})</th>
<th>Ag (Unpaired electrons)</th>
<th>Cu (Unpaired electrons)</th>
<th>Ni (Unpaired electrons)</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>CH$_3$OH</td>
<td>CH$_3$OH</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CH$_4$</td>
<td></td>
<td>CH$_3$OH</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>CH$_4$</td>
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<td>10</td>
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<tr>
<td>12</td>
<td>HO</td>
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<td>14</td>
<td></td>
<td>HO</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td>CH$_3$-CH$_3$</td>
</tr>
<tr>
<td>18</td>
<td></td>
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</tr>
</tbody>
</table>

Figure 6.10.1. Comparison of products of CO$_2$RR from Ag, Cu, and Ni.
Figure 6.10.2. Selectivity for multi-carbon products.

Figure 6.10.3 shows the partial current density of CO$_2$RR products (excluding formate and CO). For Cu, methane and ethylene partial current densities follow different trends. Methane partial current density continues to increase with increasing overpotential, but ethylene levels off. It was argued in Chapter 3, that these differences indicate that the two products have different rate determining steps. For Ni and Ag, there are not large differences in the trends followed by the single and multi-carbon products. The Tafel slopes of the products are different, but these differences are likely within error. While there must be clear differences in the pathway to single and multi-carbon products on Ni and Ag, the data in Figure 6.10.3 does not rule out the possibility that multi- and single carbon products may share a rate determining step.
Figure 6.10.3. Partial current density of CO$_2$RR products for Ag, Cu, and Ni.

### 6.11 Summary

Studying the activity of Au, Ag, Zn, Cu, Ni, Pt, and Fe for CO$_2$RR using an experimental method sensitive for minor product detection offers the most consistent and complete picture available to date of the activity of each metal over a range of potentials. Overall CO$_2$RR activity follows a volcano-type relationship based on the Sabatier principle. Au has the highest CO$_2$RR activity, suggesting it has a CO binding strength close to optimal. Unfortunately, mass transport limits CO$_2$RR at high overpotential on the best catalysts. The Tafel slopes of HER and CO$_2$RR on the metals studied were determined. Mass transport likely affects the Tafel slopes calculated, making their interpretation difficult, but values for HER were high on Ag, Zn, and Cu, likely due to competition with CO$_2$RR. CO$_2$RR tafel slopes were also high, perhaps indicative of slow kinetics.

Due to the sensitivity of the experimental setup, a number of novel CO$_2$RR products were observed. Common products shared by most of the metals were methane.
and methanol. Measurements of the potential dependence of the partial current density of methane and methanol led to the conclusion that these two products share many common mechanistic steps that differ only late in the reaction pathway, likely with C-O bond cleavage. There is a trend toward lower overpotential methane and methanol formation on metals that bind CO strongly. A strong CO-surface bond also correlated with earlier HER onset.

Cu, Ni, and Ag were the only metals that catalyzed the formation of multi-carbon products. Ag produced only oxygenates, Cu produced a mixture of hydrocarbons and oxygenates, and Ni produced only hydrocarbons. The favorability of the observed products may be related to the oxygen binding strength to the three metals. On Cu and Ni, multi-carbon products were favored at lower overpotential and single carbon products dominated at high overpotential. For Cu there were clear differences in the trends in partial current density for multi- and single carbon products, but for Ni and Ag there were not striking differences.

The insights gained demonstrate the importance of measuring CO$_2$RR activity over a range of potentials with methods capable of quantifying even minor products. The deeper understanding of known catalysts presented here can guide the search for catalysts with higher CO$_2$RR activity, such as transition metal alloys. Better CO$_2$RR catalysts would open up more alternatives to fossil fuels for electricity generation and be a source of commodity chemicals.

### 6.12 References


Chapter 7. Fe, Ni, and FeNi alloy CO$_2$RR activity

7.1 Abstract
This chapter describes the activity of Fe, Ni, and an FeNi alloy film for CO$_2$RR. Iron is a well-known Fischer-Tropsch catalyst and surface science studies have characterized the interaction of CO with both Ni and Fe surfaces. However, it is not clear how reactivity under these conditions is related to CO$_2$RR. Fe, Ni, and FeNi alloy have low current efficiency for CO$_2$RR and mainly produce hydrogen. However, alloying Fe and Ni does significantly change the activity; methane appears at a lower overpotential when using the FeNi surface, than on any of the pure metals tested to date, demonstrating that alloying can lead to increased catalyst performance.

7.2 Introduction
The comparison of the transition metals in Chapter 6 shows that Fe and Ni have the lowest partial current density for CO$_2$RR, which can be attributed to their strong CO binding energy. However, Fe does have the lowest overpotential for the production of more reduced products (hydrocarbons or alcohols) and both metals are interesting for insights into CO$_2$RR that they may provide. Besides Cu, Ni is the only other metal reported to make products with more than one carbon (ethylene and ethane). Ni has also been reported to have a higher current efficiency for hydrocarbons than any metal besides Cu.$^1$ Fe is interesting because it is commonly used for CO/CO$_2$ reduction in the Fischer-Tropsch (F-T) process (Section 1.4) which is the thermochemical analog of electrochemical CO$_2$RR. The mechanism of F-T is still actively debated, but two commonly discussed possibilities are chain growth through a) the polymerization of methylene groups on the surface or b) CO insertion into the bond between an existing hydrocarbon chain and the surface (Figure 7.2.1).$^2$
Hori et al. have studied Fe and Ni for CO$_2$RR and CO reduction and compared their activity to Cu. CO has been detected during CO$_2$RR using vibrational spectroscopy on the surface of Fe and Ni, leading to the conclusion that it is an intermediate. Ethylene, ethane, and formate have been reported as products of CO$_2$RR by Ni. CO reduction by Ni reportedly leads to the same product distribution along with a small amount of ethanol. Hori reports that CO$_2$RR on Fe leads only to HER. But in a separate study of CO reduction on Ni and Fe, many reduced compounds are reported as products of both metals. However, the similarities between Fe and Ni activity and the resemblance of the products to the products of CO reduction on Cu, leaves some doubt about the possibility of Cu contamination.

Fe and Ni have both been the subject of traditional surface science studies of adsorbed CO. Fe is known to dissociate adsorbed CO into carbon and oxygen separately bound to the surface. The rate and extent of dissociation is dependent on many factors. At low temperature, CO adsorbs molecularly to Fe and only slow rates of dissociation are seen at room temperature. A high coverage of CO or the presence of other adsorbates (ie. hydrogen) leads to more molecularly adsorbed CO than is seen on clean surfaces at low coverage. In contrast, CO molecularly adsorbs on most Ni surfaces, although CO dissociation has been observed on stepped Ni(111) crystals above 450 K.
F-T occurs at high pressure and temperature on supported nanoparticle surfaces. Surface science studies occur at low pressure on flat or single crystal surfaces. The CO$_2$RR results discussed in this chapter occur in an aqueous environment at room temperature on polycrystalline metal electrodes. Differences in experimental conditions are likely to lead to different activity, however, possible comparisons of the three different conditions will be discussed.

With knowledge of the activity of pure Fe and pure Ni in hand, the two metals were alloyed together and see how CO$_2$RR activity was affected. While the CO$_2$RR current efficiency of the FeNi alloy was low, methane formation was observed at a lower overpotential than any of the pure metals tested to date. The improved activity of the alloy catalyst demonstrates how alloying can increase activity beyond that of the pure metals and is a promising step towards a energy efficient CO$_2$RR.

### 7.3 Fe metal activity for CO$_2$RR

The same method used to characterize the activity of Cu metal for CO$_2$RR (Chapter 2) was used to characterize the activity of Fe (Alfa Aesar, 0.1mm thick, product #40493, lot #B27U015, 99.99% metals basis), with the following changes: The electrolysis cell used was made of Kel-F and cleaned in 35% nitric acid each night after use, only two electrolysis experiments were run at each potential (instead of 3+), and the surface of the iron was mechanically polished and rinsed with water before each use (no electropolishing).
Figure 7.3.1. CO$_2$RR electrolysis current on Fe.

Figure 7.3.1 shows the current drawn over the course of an hour at each potential tested. Experiments run at the same potential are shown in the same color and there is good agreement between them. Currents measured at the most negative voltages (-0.59 and -0.63 V) are quite noisy. Spikes in the current are one of the factors that limit how negative of voltage can be studied.

7.3.2. Comparison of Fe CV and average electrolysis current.
Figure 7.3.2 compares the average current measured at each of the voltages shown in Figure 7.3.1 to CVs taken before and after the application of the hour-long constant potential. Two sets of CVs are shown, one set where the potential hold was positive of -0.54 V and one set where the potential hold was negative of -0.54 V. In the case of experiments run at lower overpotentials, there is good agreement between the average electrolysis current density and the initial and final CV. Experiments run at higher overpotentials showed an increase in the current drawn during the CV after applying a constant voltage for an hour. The increase in current shown in the CV correlated to an increase in the current drawn during the hour of constant potential. The reason for the slight increase in current is unknown, but it could be caused by a slight increase electrolyte temperature as observed in the case of Cu.

![Graph showing CO$_2$RR partial current density and current efficiency for Fe.](image)

Figure 7.3.3. CO$_2$RR partial current density and current efficiency for Fe.
The products of CO\textsubscript{2}RR on Fe were measured with GC and NMR using standard procedures and only methane was detected as a product. Figure 7.3.3 shows the current efficiency and partial current density for hydrogen and methane. Nearly all of the current goes to make hydrogen, with 0.01% or less going to produce methane. Although iron has poor activity for CO\textsubscript{2}RR in terms of current efficiency, the overpotential needed for methane production is lower than Cu or any other pure metal (Figure 6.9.1).

\textsuperscript{13}CO\textsubscript{2} was reduced on Fe to look for additional products that cannot be detected with \textsuperscript{1}H NMR. No identifiable liquid phase products were observed; these results are discussed further in Appendix F. XPS spectra were collected before and after electrolysis and no metal impurities were detected in either case (Appendix D).

**7.4 Ni metal activity for CO\textsubscript{2}RR**

Ni metal (Alfa Aesar, 0.1mm thick, product #12046, lot #B11X051 and G29U009, 99.994\% metals basis) activity for CO\textsubscript{2}RR was tested in the same way as Fe (but 3+ experiments were repeated at each potential instead of 2). Figure 7.4.1 shows the current drawn over an hour at the voltages listed. As with Fe, considerable noise is present at the highest overpotentials and there is a slight increase in the absolute value of the current over the hour. Experiments at lower overpotential show a slight decrease in the absolute value of the current over the course of the hour, but the current efficiencies of the products were constant.
Figure 7.4.1. CO$_2$RR electrolysis current on Ni.

Figure 7.4.2 compares the average current drawn over the hour to the first and second sweep of a CV taken before holding the potential and one taken after. The first sweep shows an initial increase in current as the voltage goes more negative (0 to -0.5 V), but the current then plateaus (-0.5 to -0.9 V), before increasing again. Much less current is drawn in the second sweep. The first sweep of the CV is consistent with the Ni surface becoming poisoned by a CO$_2$RR intermediate that lowers the rate of HER. The surface then remains poisoned throughout the rest of the measurement because the potential never goes positive enough for the poisoning adsorbate to be oxidized away. It is likely that the adsorbate is CO because it has been detected on the surface during CO$_2$RR using vibrational spectroscopy.$^3$ CO has also been reduced on Ni and yields products similar to those of CO$_2$RR.$^6$ This suggests that CO$_2$ is first reduced to CO on a Ni surface and that CO can be further reduced to other products, but the reduction of CO is kinetically slow (rate determining step).
Figure 7.4.2. Comparison of Ni CV and average electrolysis current.

Figure 7.4.3 shows the products of CO$_2$RR on Ni in terms of current efficiency and partial current density. Hydrogen is the major product, but methane, ethane, ethylene, formate, and methanol are also observed. Interestingly, as with Fe, CO is not detected as a product. This is likely because CO binds so strongly to the surface of Fe and Ni that it does not desorb and is therefore not measured by GC. Of the CO$_2$RR products, methanol is favored, followed by methane. This contrasts with Cu (and Fe) where methane is highly favored over methanol. Also in contrast to Cu (ethylene favored over methane at lower overpotential), one carbon products (methane and methanol) are favored at all voltages over the two carbon products (ethane and ethylene). Ni binds ethylene more tightly than Cu,$^8$ so the ethane reported likely comes from the further reduction of ethylene. The current efficiencies for the CO$_2$RR products do not change very much across the potential range, suggesting that the relative rates of HER and CO$_2$RR are constant.
Figure 7.4.3. CO$_2$RR partial current density and current efficiency for Ni.
7.5 FeNi alloy activity

![Figure 7.5.1. XRD of Ni, Fe, and NiFe alloy supported on Ni foil.](image)

An FeNi alloy thin film was also tested as a CO₂RR catalyst. The film was prepared by the electrodeposition of Fe and Ni from a bath composed of 0.05 M NiCl₂ and FeSO₄ and 0.5 M NaCl onto a mechanically polished Ni foil (Alfa Aesar, 0.1mm thick, product #12046, lot #B11X051 and #G29U009, 99.994% metals basis using a potential of -0.7 V with 25 ms pulses to -4 V vs. Ag/AgCl with a pulse period of 1000 ms for a total time of 5 mins. The oxidized electrodeposited film was then reduced in a furnace under forming gas (5% H₂, balance N₂) at 450° C for 1 hr. XRD of the FeNi alloy supported on Ni foil (Figure 7.5.1) showed the formation of new peaks to the left of Ni, corresponding to alloy formation and a slight increase in unit cell size from 3.54 Å for pure Ni to 3.59 Å for the FeNi alloy. This is consistent with the formation of an FeₓNi₁₋ₓ phase. XPS of the FeNi surface (Figure 7.5.2) after reduction showed a 1:1 Fe:Ni ratio.
The activity of the FeNi alloy was tested using an abbreviated method. The cell was assembled as usual. A CV was taken and then the potential was held at the lowest overpotential to be measured. The GC was used to measure the gas phase products after 15 mins at that potential. The potential was held for a total of 18 mins and then switched to the next potential. Again, the gas phase products were measured 15 mins into the potential hold. This was repeated for all of the potentials measured. A final CV was taken and the cell disassembled. This method does not offer complete product characterization because the current efficiency of liquid products cannot be measured at distinct voltages. However, an advantage is that the same electrode is used throughout, so there are no differences in surface morphology or alloy stoichiometry between potentials due to differences in preparation.

![Figure 7.5.2. XPS of FeNi alloy compared to pure Ni and Fe.](image)
Figure 7.5.3. CO$_2$RR electrolysis current on FeNi alloy.

Figure 7.5.3 shows the current drawn at the different applied potentials and Figure 7.5.4 shows the average current density at each potential plotted with a CV taken before the start of electrolysis. The CV does not show the same deactivation plateau observed with Ni, but the average electrolysis current is less than the current seen in the CV. This could indicate a slower deactivation in the case of FeNi compared to Ni, where deactivation was observed in the first CV.

Figure 7.5.4. Comparison of FeNi CV and average electrolysis current.
Figure 7.5.5 shows the gas phase products measured. Hydrogen is the major product, but methane and ethane are also detected. The current efficiency of the products is relatively flat across the potential range and methane is favored over ethane. The next section will compare the activity of Fe, Ni, and the FeNi alloy in more detail.

![Figure 7.5.5. CO₂RR partial current density and current efficiency for FeNi.](image)

### 7.6 Comparison of Fe, Ni, and FeNi alloy

Figure 7.6.1 shows the initial CV, average electrolysis current, and partial current density for the hydrocarbon products (methane, ethylene, and ethane) of Fe, Ni, and FeNi alloy. In terms of current, the FeNi alloy shows activity between Fe and Ni and the average electrolysis current on the alloy is closer to that of pure Ni. Alloyling appears to decrease
the poisoning effect of CO$_2$RR intermediates building up on the surface that occurs on Ni.

![Graph showing comparison of Fe, Ni, and FeNi alloy](image)

**Figure 7.6.1.** Comparison of Fe, Ni, and FeNi alloy.

Looking at the identity of the products reveals that neither Fe, Ni, or FeNi produced detectable amounts of CO. This suggests that CO is bound tightly on all three surfaces. The activity of the FeNi alloy for methane formation was greater than either of the pure metals. Methane appears at -0.45 V with FeNi, which is 100 mV negative of methane onset for Fe and 300 mV negative of methane onset for Ni. Ni produces both ethylene and ethane, FeNi produces only ethane, and Fe does not make any two carbon products. The onset potential for two carbon products is the same for Ni and FeNi. For Ni, the onset of hydrocarbon formation (methane, ethylene and ethane) occurs at the
same potential, but on the NiFe alloy the onset potential for methane and ethane are offset by 300 mV.

Many of the difference in activity between the alloy and the pure metals can be explained by d-band theory. XRD of the FeNi alloy (Figure 7.5.1) shows that the alloy has a larger unit cell than pure Ni. Expansion of the lattice leads to the metal d-band orbitals moving closer to the Fermi level. The shift in the d-band causes the surface to bind adsorbates stronger than a pure Ni surface. One example of how tighter adsorbate binding changes the product distribution may be the appearance of ethane (and no ethylene) with the alloy catalyst, while both ethylene and ethane are products of CO$_2$RR on Ni. This is likely because ethylene is so tightly bound to the FeNi surface that it is fully reduced to ethane before it can desorb. On Ni, the weaker ethylene binding strength could result in some ethylene desorbing before being fully reduced and some ethylene staying on the surface until it is reduced to ethane.

While the C$_2$ product distribution is different between Ni and FeNi, the most profound difference is in the onset potential for methane formation, which is early on FeNi than on either of the pure metals. This could arise from an increase in the binding strength of CO. There is a trend toward earlier onset potential for hydrocarbon and alcohol formation as the CO binding energy increases, so if CO binding to FeNi is stronger than CO binding to Fe, the early onset potential for methane formation may be following this trend. DFT calculations suggest that CO$_2$RR on metals that bind CO strongly may follow a different reaction pathway than the weaker binding CO metals.$^{10}$ On this pathway, the limiting potential step is going from *CO $\rightarrow$*COH and the overpotential of this step decreases as CO binding gets stronger.

The above analysis holds if CO binding on FeNi is stronger than CO binding on Fe. However, d-band theory only predicts that CO binding to FeNi is stronger than CO binding to Ni and it is difficult to say without performing a DFT calculation if CO binding strength to FeNi is between Fe and Ni or stronger than either. In this case, the higher alloy activity could be explained by a pathway that goes through CO dissociation. Fe is known to dissociate CO slowly at room temperature and NiFe has been predicted by DFT to have a higher rate of CO dissociation.$^{11}$ Hopefully, future experiments in this
area to determine the CO binding energy to the FeNi alloy surface can shed light on the reason for the lower methane overpotential.

**7.7 Comparison to UHV and F-T activity**

The pure metals and alloy did not make long chain hydrocarbons as observed in F-T and Fe did not even catalyze C-C coupling, but Ni and FeNi did catalyze the formation of ethylene and ethane. No oxygenated multi-carbon products were observed on Ni, so it is not possible to rule out either mechanism pictured in Figure 7.2.1. Methanol is the main CO$_2$RR product of Ni, so at least some products do not arise from the loss of both the C-O bonds of CO$_2$. It can be stated that not all of products of CO$_2$RR on Cu arise from either of the schemes shown in Figure 7.2.1 because the products glyoxal, acetate, and hydroxyacetone could not come from those pathways. While those products were not detected when using Ni to catalyze CO$_2$RR, it is also possible that CO$_2$RR on Ni follows the same pathway was on Cu.

Under UHV surface science study conditions, CO dissociates on Fe at a slow rate at room temperature. CO$_2$RR activity of Fe (Figure 7.3.3) does not rule out the possibility that CO dissociation occurs. The partial current density for methane has no potential dependence, instead, the rate of methane production is nearly the same at all voltages where it is measured. This leaves open the possibility that a chemical step (such as CO dissociation), which does not have a potential dependent rate, is the rate-limiting step in methane formation.

Further study of Ni, Fe, and FeNi alloy is needed to determine more about the mechanism. Hori has reported ethanol as a product of CO reduction on Ni, it would be interesting to repeat that experiment and rule out the loss of all C-O bonds when C-C coupling occurs. CO reduction on Fe at higher temperatures would be interesting, because the C-O dissociation rate would be expected to increase, which would increase the amount of methane if C-O dissociation is the rate-limiting step.

**7.8. Conclusions**

The CO$_2$RR activity of Fe, Ni, and FeNi alloy was tested. None have a high current efficiency for CO$_2$RR, but hydrocarbons and/or alcohols were observed as products. Iron
produced only methane, Ni produced formate, methanol, methane, ethylene, and ethane, and FeNi made the same products as Ni, but methane appeared at a lower overpotential than either pure metal. Future experiments to determine the reason for the lower overpotential observed for the alloy are needed, but the increase in activity represents a step towards an energy efficiency catalyst for CO$_2$RR to hydrocarbons and alcohols.

### 7.9 References

Chapter 8. Conclusions and future directions

8.1 Thesis Summary

This thesis begins with the development of a custom electrolysis cell for CO$_2$RR that can be coupled to product detection by NMR and GC. This method allows for accurate voltage measurement and the quantification of minor products to give the most complete characterization of CO$_2$RR activity available to date. The CO$_2$RR activity of Cu metal is well-studied, but applications of the more sensitive experimental method lead to the identification five novel products: glyoxal, glycolaldehyde, ethylene glycol, hydroxyacetone, and acetone. The CO$_2$RR product identities and their potential dependence inspired the hypothesis that the enol and diol forms of the products may be the active intermediate species on the electrode surface. CO is believed to be an intermediate of CO$_2$RR to methane and ethylene and the direct electrochemical reduction of CO confirmed that this is the case for many of the novel products observed as well.

The activity of metals besides Cu was also explored; Au, Ag, Zn, Cu, Ni, Pt, and Fe CO$_2$RR activity have all been measure using the same experimental method. This represents the most complete dataset of transition metal activity available and reveals several important trends. A plot of CO$_2$RR activity vs. CO binding energy places Au at the top of the volcano, suggesting that it has a near optimal binding energy for CO (and other intermediates). A high CO binding energy is also correlated with an early onset potential for HER and methane/methanol formation. With knowledge of pure metal activity in hand, an FeNi alloy was synthesized and characterized for CO$_2$RR activity. Pure Ni and Fe are poor overall CO$_2$RR catalysts, but they are capable of producing hydrocarbon products. Allying Fe and Ni improved the activity by decreasing the overpotential necessary for methane formation, however, the overall activity of FeNi was still poor. The next section will discuss unanswered questions and areas for future research.
8.2 Future Research Directions

There are many areas where further research is needed. CO₂ and CO are both reduced to make a range of products. An interesting study, would be the electrochemical reduction of each of the products of CO₂RR to identify instances where an observed product is also an intermediate in the formation of a more reduced product. This has already been reported in literature to some extent. The reduction of acetaldehyde and glycolaldehyde reportedly leads to ethanol formation and the conclusion that these two compounds are intermediates on the pathway to ethanol.¹ These studies looked at only a small subset of the products and did not consider the enol or diol forms of carbonyl containing compounds; a more thorough study could fill in the identity of many intermediates in the pathway.

A pathway to multi-carbon products involving the enol and diol forms of intermediates is discussed in Chapter 2. More research is needed to assess the feasibility of this pathway. The enol form is unfavorable due to its high energy, but may be stabilized by the catalyst surface. DFT calculations of the possible intermediate forms could determine if interacting with the surface stabilizes the enol tautomer. It might also be possible to calculate the barrier to dehydroxylation to see if that step is kinetically accessible.

A key question is the nature of the C-C coupling step which leads to ethylene and the other multi-carbon products. There is debate at this time whether C-C coupling is a purely chemical step or whether it is an electrochemical step involving the transfer of only an electron or a proton and electron. If the C-C coupling step is the rate determining step in multi-carbon product formation, then understanding the pH dependence of the rate of ethylene (or other multi-carbon products) formation could shed light on the nature of this step. Hori² has suggested that the rate of ethylene formation is not dependent on pH, but methane formation is pH dependent. This suggests that the rate determining step to make ethylene is purely an electron-transfer step. Confirmation of Hori’s results is needed to strengthen support for his conclusions.

One of the most interesting products generated by CO₂ and CO reduction is acetate. It is unclear how acetate, which contains two oxygen atoms bound to the same carbon, is generated from CO, where only one oxygen is attached to the carbon.
Electrochemical reduction of acetate and possible earlier intermediates to its formation, as well as exploration of possible solution phase reactions that could occur, might shed light on the origin of acetate and the entire CO\textsubscript{2} reduction pathway to multi-carbon products.

Exploring the effect of surface morphology clearly affects the product selectivity and overpotential of CO\textsubscript{2}RR, but studies in this area have focused only on the extremes of surface structure: single crystals and extremely rough surfaces generated through oxidation followed by reduction. Experiments utilizing surfaces with controlled morphology are needed to understand how the structure of the active site plays into activity. Using nanoparticles of a single size with specific facets exposed might be used to understand how activity is effected by different sites.

Iron has the lowest overall activity for CO\textsubscript{2}RR, but it also has the lowest overpotential for methane formation. Under UHV conditions, Fe surfaces are known to dissociate C-O slowly at room temperature. C-O dissociation may also be occurring under CO\textsubscript{2}RR conditions and may be the rate limiting step in methane formation on Fe. Whether C-O dissociation is the rate limiting step for methane formation could be tested by increasing the temperature where CO\textsubscript{2}RR was carried out. The C-O dissociation rate should increase with temperature, leading to higher CO\textsubscript{2}RR partial current densities.

A comparison of all the metals studied for CO\textsubscript{2}RR shows that Au is near the top of the activity volcano. However, Au is still far from an ideal catalyst and the main product of CO\textsubscript{2}RR on Au is CO. A lower overpotential route to hydrocarbons may be found by designing materials with a CO binding energy between that of Cu and Au, but the necessary overpotential is still likely to be too high to be cost-effective. To make more active catalysts, the scaling relations between intermediates in the rate-determining step need to be changed. Several methods, including the use of alloys have been suggested to accomplish this goal.

Appendix A. Electrolysis cell development

Since there is no standard electrolysis cell used for reducing CO$_2$, a custom cell needed to be designed. The initial cell used (Figure A.1), consisted of flask with many necks that could be sealed with Teflon stoppers which were modified to hold the necessary electrodes and CO$_2$ purge lines. CO$_2$ reduction experiments run in this cell showed considerably lower product yields (Figure A.2) than expected based on previous reports.$^1$

Figure A.1. Original electrolysis cell design
Although it was difficult to pin down the exact reason for poor performance, this cell design has several obvious drawbacks. The electrolyte volume is relatively large (60 mL) compared to the electrode area (~4 cm$^2$), making it difficult to achieve a detectable concentration of liquid phase products. In addition, the counter and working electrodes are not separated in any way, so products generated at the working electrode can diffuse to the counter electrode and be reoxidized, lowering the concentration of CO$_2$ reduction products present and opening up the possibility that a product could be partially oxidized at the counter electrode and the final, oxidized form mistaken for a direct product of CO$_2$ reduction. In addition, CO$_2$ diffusion to the electrode surface is likely slow and the poor kinetics of CO$_2$ reacting with water to form bicarbonate likely lead to poor buffering and large pH changes.

The next generation of cell design solved many of these problems (Figure A.3). The volume is significantly smaller, around 15 mL with a similar electrode surface area (~4 cm$^2$). The working and counter electrodes are separated from one another by an ion exchange membrane. The main drawback is the positioning of the CO$_2$ inlet on the top side of cell, necessitating that the inlet tube extend down through the electrolyte to get adequate purging. The tube is positioning likely affects mass transport and the electric field between the electrodes. To reduce CO$_2$, the cell was first purged, then sealed and a potential applied. After an hour, a syringe was used to take a sample of the head space and the gas injected into the GC and the current

![Figure A.2. Current efficiency achieved with cell shown in A.1](image)
efficiency for the gas phase products determined. This procedure gave even worse current efficiencies than observed with the first generation cell (<1% CO$_2$RR), perhaps because the interfacial area of the CO$_2$ headspace and the aqueous electrolyte was smaller, leading to worse mass transport.

The final cell design which was used with only minor changes for the CO$_2$ electrolysis experiments is discussed in Section 2.4. The electrolyte volume has been reduced even further to 9 mL and the electrode area is 5.87 cm$^2$. To achieve the CO$_2$RR results that are reported in literature, it was necessary to purge CO$_2$ constantly through the cell, presumably to get better mass transport. The CO$_2$ inlet positioning at the bottom and the outlet positioning at the top make it easy to purge through the cell in the final design.

Appendix B. Relevant current density for solar fuels

In the area of solar fuels, the energy of solar radiation is utilized to drive redox reactions for the synthesis of fuels. For example:

\[ 2H^+ + 2e^- \rightarrow H_2 \ (E_0 = 0.00 \text{ V/RHE}) \]

or

\[ \text{CO}_2 + 6H^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \ (E_0 = +0.05 \text{ V/RHE}) \]

For large scale solar fuel synthesis, water oxidation is the ideal source of the protons and electrons needed for the fuel-synthesis (reduction) reactions above, as water is inexpensive and abundant.\(^6\)\(^7\)

\[ 2\text{H}_2\text{O} \rightarrow 2\text{O}_2 + 4\text{H}^+ + 4e^- \ (E_0 = +1.23 \text{ V/RHE}) \]

A current density of -10 mA·cm\(^{-2}\) for solar fuels synthesis is relevant because this current density roughly matches the spectrum for a 10\% efficient solar-to-fuels device. Here, it is shown how to arrive at this value:

1) In a collaborative effort, the photovoltaics (PV) industry, government laboratories, and the American Society for Testing and Materials (ASTM) defined the standard terrestrial solar spectrum: AM1.5G.\(^8\) Integration of this spectrum yields a value of 1000 W·m\(^{-2}\) = 100 mW·cm\(^{-2}\), an illumination intensity which is typically referred to as “1 sun”.

2) Note that the red-ox potentials above for fuel synthesis and water oxidation are approximately 1.2 V apart. If 1 sun = 100 mW·cm\(^{-2}\) = 100 (mA·V)·cm\(^{-2}\), then a 100 \% efficient solar-to-fuel device would draw \((100 \text{ (mA·V)·cm}^{-2})/(1.2 \text{ V}) = 83 \text{ mA·cm}^{-2}\) under AM1.5G.

3) A 10 \% efficient solar fuels device would draw 1/10\(^{th}\) the current, at 8.3 mA·cm\(^{-2}\).
Appendix C. Standard reduction potentials of CO$_2$RR half reactions

Finding the standard reduction potentials of an electrochemical reaction is a simple calculation. To find the reduction potential for CO$_2$, one must first know the reduction and oxidation potential of water, which is 1.23 V. The calculation for methane and formate is shown below (the values of Gibbs free energy (from tabulated data)$^{1,2}$ are given in Joules, Faraday’s constant has units of Coulombs/mole of electrons):

1) Write the overall reaction, which is the sum of the two half reactions:
   \[ \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2 \]

2) Calculate the Gibbs free energy of formation ($\Delta G$):
   \[
   \begin{align*}
   G(\text{Products}) - G(\text{Reactants}) &= G(\text{CH}_4) + \frac{1}{2} G(\text{O}_2) - G(\text{H}_2\text{O}) - G(\text{CO}_2) \\
   &= (-50.75) + 2*(0) - (-394.36) - 2*(-237) \\
   &= 817.91
   \end{align*}
   \]

3) Calculate the cell potential:
   \[
   \Delta E^\circ_{\text{cell}} = \frac{\Delta G}{-nF} = \frac{817910}{-8*96485} = -1.06 \text{ V}
   \]

4) Split into 2 half reactions:
   \[
   \begin{align*}
   \text{CO}_2 + 8\text{H}^+ + 8e^- &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
   6\text{H}_2\text{O} &\rightarrow 2 \text{O}_2 + 8\text{H}^+ + 8e^-
   \end{align*}
   \]

5) Since $E^\circ_{\text{H}_2\text{O}/\text{O}_2}$ is 1.23, so:
   \[
   \Delta E^\circ_{\text{cell}} = E^\circ_{\text{CH}_4} - E^\circ_{\text{O}_2} \text{ and } E^\circ_{\text{CH}_4} = 0.17 \text{ V}
   \]

6) Then use the Nernst equation to correct for different pHs:
   \[
   E = E^\circ - RT/nF \ln([\text{Red}] / [\text{Ox}])
   \]
   For $\text{H}^+/\text{H}_2$:
   \[
   E = 0.17 - 8.314*298/(2*96485) \ln ([\text{CH}_4][\text{H}_2\text{O}^2]) / ([\text{CO}_2][\text{H}^+])^8 \\
   = 0.17 - 2.3*8*8.314*298 / 8*96485 \log [\text{H}^+] \\
   = 0.17 - 0.059 * \text{pH}
   \]
Despite the simplicity of the above calculation, there are differences in the reduction potential values reported by different authors.\textsuperscript{3-6} One source of disagreement is what the actual reactant is. Some authors have not used the $\Delta G(CO_2)$ to calculate the reversible potential, but instead used $\Delta G(H_2CO_3)$, $\Delta G(HCO_3^-)$, or $\Delta G(CO_3^{2-})$, depending on which is most stable at a given pH.\textsuperscript{5} Table C.1 shows the standard reduction potential of $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ using the different species of $CO_2$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^o CO$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2 \rightarrow CO$</td>
<td>$-0.1$ V</td>
</tr>
<tr>
<td>$H_2CO_3 \rightarrow CO$</td>
<td>$-0.06$ V</td>
</tr>
<tr>
<td>$HCO_3^- \rightarrow CO$</td>
<td>$0.13$ V</td>
</tr>
<tr>
<td>$CO_3^{2-} \rightarrow CO$</td>
<td>$0.43$ V</td>
</tr>
</tbody>
</table>

Table C.1. Change in reversible potential if different reactant is used

Another source of differences is what form of the product $\Delta G$ refers to. For a product like methane, it is relatively straightforward. The $\Delta G$ value for gas phase $CH_4$ is used. However, some of the liquid phase products, it is more complicated. Formate is potentially the worst, because it is not clear whether it is most correct to use the value for $\Delta G$(pure liquid HCOOH), $\Delta G$(aqueous $1 \text{ M HCOOH}$), or $\Delta G$(aqueous $1 \text{ M HCOO}^-$). Using the different values leads to reduction potentials of -0.17 V, -0.11 V, and -0.22 V, respectively. In this work, the value for $\Delta G$(aqueous $1 \text{ M HCOO}^-$) is used to calculate the reduction potential, since the formate generated will stay in solution and at the electrolysis pH it will be deprotonated. Acetate is similar to formate in that it is also deprotonated at pH 6.8, so the $\Delta G$ value used referred to the $1 \text{ M ionic form in aqueous soln.}$ For the other liquid phase products, the values of $\Delta G$ used referred a $1 \text{ M concentration of the product when available, however, in cases where that value could not be found, the value of the pure liquid product was used.}$

It is common to put electrochemical data on an RHE scale so that data taken at different pHs can be easily compared. For most products, their reduction potential pH independent on this scale because the reduction potential shifts with $59 \text{ mV/pH unit, which is the same as HER, which is defined as zero regardless of pH on the RHE}$
scale. However, two products, acetate and formate, do not shift in potential 59 mV/pH unit. Instead, the reduction potential of these products shifts 30 mV/pH. For these products, there is one more proton than electron transferred during the reaction, leading to a different Nerstian shift than HER. This means that on an RHE scale, the reduction potential of acetate and formate is not constant, nor would it be for any ionic product. Figure C.1 shows the reversible potential as a function of pH for selected products of CO₂ reduction. For comparison, acetic acid and formic acid are also shown, although at pHs above 5 they would be unstable.

Figure C.1. Reversible potential of selected CO₂RR products on an RHE scale

Appendix D. Minimizing metal impurities

It has been suggested that metal impurities are the cause of the CO$_2$RR activity in some irreproducible studies.\textsuperscript{1} Efforts were taken to minimize metal impurities so that CO$_2$RR results reported would be truly representative of the activity of the transition metals studied. All metal foils were purchased from Alfa Aesar and were of the highest purity available. Cu was considered the worst metal impurity because of its high activity hydrocarbon formation during CO$_2$RR. Table D.1 shows the product and lot number for each metal, as well as the Cu concentration in each. Cu is present at the ppm level (as are many metals). Assuming the Cu impurities in each metal have the same CO$_2$RR partial current as bulk Cu, then the partial current density for the major products, methane and ethylene, would be 31 nA and 8 nA, which are below the detection limit for CO$_2$RR products.

<table>
<thead>
<tr>
<th>Product #</th>
<th>Metal</th>
<th>lot #</th>
<th>ppm Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>12046</td>
<td>Ni</td>
<td>B11X051</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>G29U009</td>
<td>1.6</td>
</tr>
<tr>
<td>12126</td>
<td>Ag</td>
<td>D22W016</td>
<td>&lt;10</td>
</tr>
<tr>
<td>11915</td>
<td>Zn</td>
<td>J08S021</td>
<td>&lt;1</td>
</tr>
<tr>
<td>40493</td>
<td>Fe</td>
<td>B27U015</td>
<td>2</td>
</tr>
<tr>
<td>11391</td>
<td>Au</td>
<td>C01Y014</td>
<td>&lt;2</td>
</tr>
<tr>
<td>42456</td>
<td>Pt</td>
<td>J19R006</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table D.1. Cu impurity levels in metal foils used in CO$_2$RR.

Additionally, to avoid cross-contamination between experiments performed on different metals, either dedicated polycarbonate electrolysis cells or Kel-F electrolysis cells washed in nitric acid were used for CO$_2$RR. The use of the anion exchange membrane between the counter and working electrodes prevented dissolved Pt from counter electrode from reaching the working electrode compartment and depositing on the working electrode. XPS was used to confirm that metal impurities before and after CO$_2$ electrolysis were below the detection limits of the technique (Figure D.1).
Figure D.1. XPS on metal electrodes before and after CO$_2$ electrolysis.

Appendix E. Metal sulfide catalyzed CO$_2$RR

Taking inspiration from the enzyme carbon monoxide dehydrogenase (CODH),\textsuperscript{1} we explored the CO$_2$ reduction activity of Fe$_4$S$_4$ cubanes supported on highly oriented pyrolytic graphite (HOPG). While we were successful in attaching the cubanes to the surface and visualizing them with STM, XPS spectra taken before and after water exposure showed that the Fe$_4$S$_4$ complexes were unstable (Figure E.1).

Figure E.1. A) STM of cubanes attached to an HOPG surface with XPS showing changes to the Fe and S signal
We then moved on to exploring thin films of other sulfides. CO$_2$ electrolysis experiments were performed with thin films of FeS$_2$, FeS, MoS$_2$ and VS$_2$. Again, the Fe-S materials were unstable (Figure E.1B) and hydrogen was the major product detected during CO$_2$ reduction. MoS$_2$ is a well known catalyst for hydrogen evolution$^{2,3}$ and produced mostly hydrogen, as did VS$_2$. Figure E.2 shows that hydrogen was produced at high current efficiency at a range of potentials on the sulfides studied.

![Figure E.2. Current efficiency of H$_2$ production during CO$_2$RR experiments on sulfides.](image)

Appendix F. $^{13}$C NMR peaks

$^{13}$CO$_2$ was reduced in the standard experimental setup on Cu and $^{13}$C NMR run overnight on a sample of the electrolyte containing 5% D$_2$O and the internal standards phenol and DMSO. Most of the peaks belonged to known CO$_2$RR products. Glyoxal was the only product identified solely based on the $^{13}$C NMR spectra. Table F.1 shows the position and height of peaks in the $^{13}$C spectra with assignments. Highlighted in yellow are the few peaks that could not be identified. Some of them appeared as doublets, as indicated along with the J-coupling constant. The unknown peaks are mostly small, but the peak at 125.39 ppm is reasonably sized. This peak also appears after $^{13}$CO$_2$ reduction by other metals, including Ni and Fe. There are not many chemicals with shifts in this area, so the peak may be an artifact of some kind. It appears near, but not exactly at, the center of the spectrum. More experiments will be needed to determine if this peak is an artifact or if it is real, what compound it corresponds to.
<table>
<thead>
<tr>
<th>(ppm)</th>
<th>Height</th>
<th>Identification</th>
<th>J Coupling</th>
<th>(ppm)</th>
<th>Height</th>
<th>Identification</th>
<th>J Coupling</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.0062</td>
<td>CH₃CH₂CH₂OH</td>
<td>88.88</td>
<td>0.0007</td>
<td>doublet</td>
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<td>44.3</td>
</tr>
<tr>
<td>10.48</td>
<td>0.006</td>
<td>CH₃CH₂CH₂OH</td>
<td>89.24</td>
<td>0.0008</td>
<td>doublet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.47</td>
<td>0.0317</td>
<td>CH₃CH₂OH</td>
<td>90.41</td>
<td>0.0023</td>
<td>Glycolaldehyde</td>
<td>48.9</td>
<td></td>
</tr>
<tr>
<td>17.62</td>
<td>0.0025</td>
<td>CH₃CH₂OH</td>
<td>90.79</td>
<td>0.0023</td>
<td>Glycolaldehyde</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.76</td>
<td>0.0349</td>
<td>CH₃CH₂OH</td>
<td>91.4</td>
<td>0.0063</td>
<td>Glyoxal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.8</td>
<td>0.001</td>
<td>CH₃COO⁻</td>
<td>3.53</td>
<td>96.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃COO⁻</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.83</td>
<td>0.0008</td>
<td>doublet</td>
<td>115.92</td>
<td>0.003</td>
<td></td>
<td>b) see below</td>
<td></td>
</tr>
<tr>
<td>24.15</td>
<td>0.0009</td>
<td>doublet</td>
<td>116.26</td>
<td>0.0035</td>
<td>Phenol?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.24</td>
<td>0.0048</td>
<td>CH₃CH₂CH₂OH</td>
<td>121.24</td>
<td>0.0009</td>
<td>Phenol?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.1</td>
<td>0.0049</td>
<td>CH₃CH₂CH₂OH</td>
<td>125.39</td>
<td>0.0287</td>
<td>singlet</td>
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<td></td>
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<tr>
<td>25.39</td>
<td>0.0043</td>
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<tr>
<td>30.76</td>
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<td>10.6</td>
<td>137.79</td>
<td>CH₂CH₂OH</td>
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<td></td>
</tr>
<tr>
<td>30.84</td>
<td>0.0008</td>
<td>a) see below</td>
<td>161.16</td>
<td></td>
<td>1 HCO₃⁻</td>
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<td></td>
</tr>
<tr>
<td>49.76</td>
<td>0.007</td>
<td>CH₃OH</td>
<td>171.7</td>
<td>0.001</td>
<td>HCOO⁻</td>
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<td></td>
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<tr>
<td>58.15</td>
<td>0.0295</td>
<td>CH₃CH₂OH</td>
<td>171.74</td>
<td>0.0015</td>
<td>HCOO⁻</td>
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<tr>
<td>58.3</td>
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<td>CH₃CH₂OH</td>
<td>171.76</td>
<td>0.0443</td>
<td>HCOO⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58.44</td>
<td>0.0292</td>
<td>CH₃CH₂OH</td>
<td>171.78</td>
<td>0.0016</td>
<td>HCOO⁻</td>
<td></td>
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<td>62.22</td>
<td>0.0007</td>
<td>singlet</td>
<td>171.79</td>
<td>0.0012</td>
<td>HCOO⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63.26</td>
<td>0.003</td>
<td>CH₃CH₂CH₂OH</td>
<td>171.82</td>
<td>0.0008</td>
<td>HCOO⁻</td>
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<tr>
<td>63.41</td>
<td>0.0027</td>
<td>CH₃CH₂CH₂OH</td>
<td>173.93</td>
<td>0.0007</td>
<td>OC(=O)C(=O)O⁻</td>
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</tr>
<tr>
<td>63.61</td>
<td>0.004</td>
<td>CH₂CH₂OH or HOCH₂CH₂OH</td>
<td>181.99</td>
<td>0.0015</td>
<td>CH₃COO⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64.29</td>
<td>0.0062</td>
<td>CH₃CH₂CH₂OH</td>
<td>182.41</td>
<td>0.0008</td>
<td>small</td>
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<td></td>
</tr>
<tr>
<td>64.58</td>
<td>0.0061</td>
<td>CH₃CH₂CH₂OH</td>
<td>193.23</td>
<td>0.0007</td>
<td>small</td>
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<tr>
<td>65.18</td>
<td>0.0029</td>
<td>CH₃CH₂CH₂OH</td>
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<td></td>
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<tr>
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<td>0.0026</td>
<td>CH₃CH₂CH₂OH</td>
<td>217.22</td>
<td>0.0009</td>
<td>(CH₃)₂C=O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Acetone, acetaldehyde, or propionaldehyde
b) n-Propanol or phenol

Table F.1. $^{13}$C peaks resulting from $^{13}$CO$_2$RR on Cu.
Appendix G. Hg Capture

In collaboration with Prof. Jen Wilcox and Dr. Shela Aboud of the Energy Resources Department at Stanford University (theory) and the Electric Power Research Institute (EPRI), experimental and theoretical investigations were carried out to assess the limitations associated with Hg\(_0\) capture on Au-plated screens, a process termed Mercury Capture by Amalgamation Process (MerCAP\(^\text{TM}\)). EPRI tested screens exposed to real flue gas downstream of an FGD unit from a full-scale power plant (Stanton Station, North Dakota) in addition to those exposed to a simulated flue gas from a bench-scale set-up under specific conditions. It was found that the Au coated screens worked well for Hg\(_0\) capture at the bench-scale, but not at the full-scale. The goal of this project was to determine the aspects that limited the success of MerCAP\(^\text{TM}\) at the larger scale. Below is a description of the experimental analysis performed on Au-plated screen samples prepared by EPRI.

Studies were initiated on three different full-scale tested MerCAP samples: a “fresh” sample that had never been tested, a “used” sample that had been exposed to real flue gas, and a “regenerated” sample that had been etched in nitric acid after exposure to real flue gas. By eye, the “fresh” sample is shiny, the “used” Au mesh looks to be coated with a dark, powdery film, and the “regenerated” sample appears shiny much like the “fresh” Au. The higher magnification of the SEM offers a more detailed view of the sample surfaces. The surface of the “used” sample is in fact blocked by particulates, later determined by XPS to be organic in nature. The “regenerated” sample also contains organic deposits, but of a very different morphology. Clearly, the nitric acid regeneration process does not return the Au surface to its original condition.
A strong C signal and a weak Si signal identify the deposits to be organic in nature. The “used” surface exposed to the real flue gas has a very high Hg content, while the “regenerated” surface shows only trace amounts of Hg, indicating that the regeneration process is effective in removing most of the Hg. The Hg that remains is likely trapped in the organic deposits and therefore more difficult to remove than Hg adsorbed to only the Au surface. Studies on the S signal indicate that S on the “used” sample was predominantly oxidized (SO\textsubscript{x}) while the S on the “regenerated” sample was predominantly reduced (sulfide). The regeneration process, however, removes most of the S present on the surface.

Figure G.1. SEM images of full-scale samples, a) unused clean surface, b) used surface covered in deposits, c) regenerated surface showing remaining deposits.

Figure G.2. Some XPS of Au surfaces from the full-scale experiments. a) comparison of Hg peaks in the used and regenerated samples showing that regeneration removes most of the Hg b) S peaks associated with the oxidized, higher binding energy SO\textsubscript{x} and the reduced, lower binding energy S\textsuperscript{2-}.
XPS is a surface sensitive technique, but by milling away the surface with Ar+ ions and repeating the process of scanning at various intervals, it is possible to probe the composition deeper into the surface. The organic deposits and the Au surface are milled simultaneously and at different rates, so it is difficult to deconvolute the compositions of these distinct areas from each other. From looking at the data from spots where not very much of the organic deposit is present, it is possible to say that the Hg is only present on the Au surface, not deeper into the Au film. The organic deposits likely capture Hg within the entire deposit, not just at its surface.

![Figure G.3. Depth profile of the used sample showing that the Hg doesn’t penetrate deeply into the Au.](image)

In order to try and more clearly understand the role of the organic deposits and how their presence changed the Hg capture process, additional bench-scale experiments were run with several different compositions of simulated flue gas composed of CO₂, H₂O, O₂, N₂, and varying amounts of SO₂, HCl, and Hg⁰ at 130° F. SEM analysis of the bench-scale samples shows no organic deposits on the surface. The images do show that the film peels away from the stainless steel underneath in the simulated flue gas, especially when HCl is present in the stream.
The surface composition of each of the bench-scale samples was analyzed with XPS. Even on samples where Hg was expected, none or very little was detected. There is S present in both oxidized and reduced forms. Cl appears on many of the surfaces, sometimes on samples that should not have been exposed to HCl, suggesting possible contamination. The bench-scale samples show a much smaller C and O surface composition than the Au films exposed to real flue gas in the full-scale experiments, as expected since the large C and O signals from the full-scale experiments likely came from the organic deposits.

Figure G.4. SEM images of representative bench-scale samples. a) Au film is peeling, b) Breaks in the film allow the steel underneath to be oxidized, c) Nitric acid rinsed film, d) and e) bench-scale flue gas exposure does not lead to organic deposits as on f) “used” sample from full-scale experiments. Scale bars are 200 μm.

The major difference between samples was the build-up of organic material on the full-scale samples that did not occur on the bench-scale. These organic deposits cover the Au surface so that it cannot adsorb Hg and are likely the reason that Hg capture failed to occur on the full-scale level. The difference in outcomes between the full- and bench-scale suggest that not all flue gas components are present during the bench-scale experiments and that better bench-scale testing procedures should be developed to accurately assess how well a material will capture Hg at the full-scale level.
Appendix H. Metal Support Activity

The activity of titanium foil, aluminum foil, graphite foil, and degenerately doped silicon were preliminarily tested for their CO$_2$RR activity in order to identify a material with low background activity to act as a support for nanoparticles of another metal or as part of an electrolysis cell (current collector in the GDE cell). Each material was setup in the electrolysis cell using the standard protocol. Then potential was held at sequentially higher values for 20 mins each and the gas effluent from the cell sample near the end of the 20 mins to identify the gas phase CO$_2$RR products. Figure H.1 shows the average current drawn by each material at the indicated voltage. The materials had low activity for CO$_2$RR, producing mostly CO with less than 5% current efficiency. Silicon has the lowest electrochemical activity overall, followed by Al, graphite, and Ti.

![Figure H.1. Average electrolysis current of materials with low CO$_2$RR activity.](image-url)
Appendix I. Comparison of metal RDE CVs

Using a rotating disk electrode (RDE) setup with solid disks of each metal, CVs were collected in 0.1 M KHCO$_3$ (CO$_2$ purged, pH 6.8), 0.1 M potassium phosphate (CO$_2$ purged, pH 6.2), and 0.1 M potassium phosphate (N$_2$ purged, pH 6.8) while rotating at 1600 rpm (Figure I.1). Tafel plots are shown to the right of the CVs. Unfortunately, there are no clear changes in slope that would indicate the onset of CO$_2$RR. There is curvature in many of the Tafel plots, but the formation of bubbles at higher current densities on the RDE surface may be responsible. Figure I.2 plots the potential needed to reach -1 mA/cm$^2$ of current on each of the metals under the three different conditions. Unfortunately, there is no clear trend that would make it possible to identify a metal as a good CO$_2$RR catalyst by looking at the CVs alone. On all the metals, the current density was generally higher in 0.1 M potassium phosphate when no CO$_2$ was present, the next highest currents occurred in 0.1 M potassium phosphate with CO$_2$, and the lowest currents occurred in 0.1 M KHCO$_3$. This suggests that CO$_2$RR had an inhibiting effect on HER. It makes sense that if the rate of CO$_2$RR is slower than HER, then less current would be drawn on a metal performing CO$_2$RR instead of HER. And on metals that are poor CO$_2$RR catalyst (Fe, Ni, and Pt), there is evidence that HER sites on the surface are blocked by CO (or another CO$_2$RR intermediate), which would lower the observed current by lower the available surface area for HER.
While all metals draw lower currents in the presence of CO$_2$, the amount of change is different depending on the metal. Fe and Zn show little change in current between the CO$_2$ and N$_2$ purged phosphate electrolyte. A possible explanation, is that at the CV potentials, little CO$_2$RR is occurring. Ni and Pt show the largest differences in voltage between CO$_2$ and N$_2$ purged solutions. Pt (and Ni to a lesser extent) is an excellent HER catalyst, but it is poisoned by CO during CO$_2$RR. Cu, Au, and Ag
show similar differences in voltage. These metals are known to be ‘good’ CO\textsubscript{2}RR catalysts, but the lower current suggests that CO\textsubscript{2}RR is slower than HER on these surfaces. Another possibility is that the active site of CO\textsubscript{2}RR is larger than needed for HER, so the same geometric area leads to a lower number of active sites for CO\textsubscript{2}RR and therefore a lower current. A result of the differences in current inhibition between the metals leads to the ordering of catalyst activity changing in the different electrolytes. Au is a poor HER catalyst (lower current than most metals in N\textsubscript{2} purged 0.1 M phosphate buffer), but it shows the highest activity in CO\textsubscript{2} purged 0.1 KHCO\textsubscript{3}. Fe is a poor HER and CO\textsubscript{2}RR catalyst. Perhaps because it does not perform much CO\textsubscript{2}RR, HER current on Fe is less affected than other metals and in CO\textsubscript{2} purged solutions it shows high activity.

While the pH of CO\textsubscript{2} purged 0.1 M KHCO\textsubscript{3} and potassium phosphate are very similar, phosphate is a better buffer than KHCO\textsubscript{3}, so the electrode surface pH is likely closer to the bulk solution pH when the phosphate buffer is used. Lower proton activity in KHCO\textsubscript{3} likely leads to lower current than is observed in CO\textsubscript{2} purged phosphate. CO\textsubscript{2}RR may also be affected differently by the phosphate and bicarbonate/carbonate anions. Unfortunately, using a N\textsubscript{2} purged KHCO\textsubscript{3} electrolyte is not completely CO\textsubscript{2} free (because the bicarbonate can decompose to OH\textsuperscript{-} and CO\textsubscript{2}).

Figure I.2. Voltage @ -1 mA/cm\textsuperscript{2} current density in different electrolytes.
The pH is also uncertain because bicarbonate decomposition leads to more OH\textsuperscript{-}, raising the pH. The decomposition of bicarbonate is kinetically slow, but at infinite time, a N\textsubscript{2} purged 0.1 M KHCO\textsubscript{3} solution will be converted to 0.1 M KOH.
Appendix J. H$_2$O vs D$_2$O electrolyte

CO$_2$RR activity on Cu was also tested using 0.1 M potassium bicarbonate in D$_2$O electrolyte to see if using the heavier deuterium isotope would change the selectivity between CO$_2$RR products or HER. Figure J.1 shows that the current drawn in a series of electrolysis experiments in D$_2$O was less than the current drawn when H$_2$O based electrolyte was used. The D$_2$O used was not as pure as the usual water from a Millipore system, so impurities could play a role in the lower current, but HER could also be slower in D$_2$O.

![Figure J.1. Current density of CO$_2$RR on Cu in H$_2$O and D$_2$O.](image)

The partial current densities of the gas phase CO$_2$RR products are shown in Figure J.2. Methane and ethylene are the major products at lower overpotentials, but HER takes over as the major product at the highest overpotentials tested. Because there was a lower current density in D$_2$O, it was possible to run experiments at much higher overpotential. If experiments in H$_2$O were taken out to the same overpotential, then hydrogen may have been the dominant product there as well.
The ratio of ethylene:methane did not change (Figure J.3). This was interesting, because there is speculation that the rate-determining step in ethylene formation maybe C-C coupling, the rate of which should not be affected by the deuterium. The rate-determining step in methane formation is probably a proton-electron transfer, which would most likely be slower in the case of deuterium. The fact that the ratio of the products didn’t change suggests that both of their rate-determining steps were equally affected by the deuterium. However, there are other possibilities, such as a change in the rate-determining step in D₂O vs H₂O. It should also be noted that shifting the D₂O results to an RHE scale was done by taking the pH and making corrections for pD.¹

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1. Reference or note.
Figure J.3. Ratio of ethylene to methane in D$_2$O and H$_2$O.